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## RARE EARTH DISTRIBUTIONS IN THE MARINE ENVIRONMENT

by

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September 1965

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RARE-EARTH DISTRIBUTIONS  
IN THE MARINE ENVIRONMENT

by

REGINA VOLFOVSKY SPIRN

M.S., The Hebrew University of Jerusalem  
(1958)

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ABSTRACT

A procedure for determination of the rare earth elements and yttrium utilizing tracer-monitored group separation, neutron activation and carrier-free partition chromatography has been developed. It is applicable over a wide range of concentrations and materials.

Using this procedure a survey of rare earths and yttrium (=RE) abundances in different types of matter from the marine environment was made. The RE were determined in 24 samples of marine materials: whole-core samples of red clay and diatomaceous ooze from the Indian and Antarctic oceans, clay fractions and calcareous tests fractions from an Equatorial Atlantic core of globigerina ooze; samples of calcareous sediment, oölite, snail shell, the body of a clam, a sword-fish vertebra and a manganese nodule; and samples of deep Atlantic filtered sea-water, the suspended solids filtered out of it, and the undialyzable fraction of similar sea-water. A sample of Alnö (Norway) carbonatite was analyzed likewise for comparison with calcareous materials of marine origin. The RE distributions in these samples and in the limited number of marine and sedimentary materials in which RE distributions had been determined previously were compared. The majority of whole-core RE distributions are

rather uniform, but in core components of different genesis they are different. More than half the RE content of marine clay is apparently adsorbed on the clay particle surfaces, and the distribution of the adsorbed RE can be quite different or quite similar to that in the interior. The RE content in calcareous parts of organisms varies over more than an order of magnitude and the possibility was indicated that in fresh calcareous structures the larger part of the RE occurs in the organic components and that in sedimented old calcareous material a great part of the RE content is post-depositionally adsorbed. RE distributions in live organic matter appear to differ greatly from those in old organic remains. The RE content and abundance pattern in the analyzed oölite are very different from those in the globigerina tests. Many materials of organic origin are selectively enriched in yttrium relative to the other heavy RE. The manganese nodule analyzed is selectively depleted in yttrium and enriched in cerium. The four complete nodule RE patterns now known vary in slope and/or curvature. The RE abundance pattern in solids ( $>0.45\mu$ ) suspended in sea-water differs noticeably from that in the water. A considerable part of the RE in filtered sea-water occurs in an undialyzable form.

The variations found indicate the scope and interest in the study of the geochemistry of RE in the sedimentary cycle in general and in the marine environment in particular. They also show that the existing data are insufficient for meaningful generalizations.

Methods of presentation of RE distributions are critically compared and a criterion for evaluation of the quality of RE analyses is proposed. A numerical index for characterization of the degree of fractionation in RE assemblages is proposed and its usefulness in revealing differences and measuring differences of RE distributions is shown.

Thesis supervisor:

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TABLE OF CONTENTS

	Page
ABSTRACT	ii
LIST OF TABLES	vii
LIST OF FIGURES	viii
 PART I	
RARE EARTH DISTRIBUTIONS IN THE MARINE ENVIRONMENT	
1. Introduction	2
2. Experimental	5
2.1 Preparation of Samples for Analysis	5
2.1.1 Unfractionated Samples	5
2.1.2 Fractionation of Core, Shell and Sea-Water Samples for RE Analysis of Distinct Constituents	7
2.2 Analytical Procedures	13
2.2.1 Sample "Opening" and RE Group Separation, Procedure A (Silicates)	14
2.2.2 Procedure B (Carbonates)	15
2.2.3 Modified Sample Dissolution or RE Group Separation Procedures	16
3. Results and Discussion	22
3.1.1 Analytical Results	22

	Page
3.1.2 Graphic Presentation of RE Data	29
Proposal of a Graphic Criterion of Reliability of RE Values	34
3.2 General Remarks on RE in the Sedimentary Cycle	60
3.3 Distributions of RE in the Marine Environment	69
3.3.1 Three Pelagic Red Clays and a Diatomaceous Ooze	72
3.3.2 Discussion of Twelve Marine Sediment Samples with Very Similar RE Patterns	80
3.3.3 Results of EDTA-treatment of "Red Clays" V2 and V9 (Attempt at Differentiation between Hydrogenous and Terrigenous RE)	87
3.3.4 Insoluble and Globigerina Tests Samples from Globigerina Ooze Core A180-74	92
3.3.4a RE in EDTA-treated Clays from Core A180-74	94
3.3.4b RE in Globigerina Tests from Core A180-74	100
3.3.5 Cariaco Trench Sediment	110
3.3.6 Oölite	112
3.3.7 Shell of <u>Polynices Heros</u> Snail	117
3.3.8 Body of Quahog Clam	118
3.3.9 Bone of Sword-Fish	122

	Page
3.3.10 Manganese Nodule	123
3.3.11 Atlantic Deep Sea-Water Fractions	128
3.3.12 AlnO Carbonatite	132
3.4 Concluding Remarks	133
Acknowledgements	136
References Cited	137
PART II	
APPENDIX A A REVIEW OF SOME ADDITIONAL LITERATURE	145
APPENDIX B THEORETICAL CONSIDERATIONS ON THE BEHAVIOR OF Ce and Eu IN THE MARINE ENVIRONMENT	153
APPENDIX C ADDITIONAL EXPERIMENTAL DETAILS	
Chemical Yields of Ce <sup>139</sup> and Y <sup>88</sup> in RE Group Separations	159
Details on Assignment of Some Blank Values	160
APPENDIX D	
Acknowledgements	162
Biographical Note	165

LIST OF TABLES

Table		Page
1	List of Samples Analyzed	48
2	Rare Earth Abundances in Red Clays, in Diatomaceous Ooze, in Products of EDTA-treatment of Red Clays, and in the Average of 17 Chondrites	23
3	Rare Earth Abundances in EDTA-treated Clays and in Globigerina Tests from Core A180-74	25
4	Rare Earth Abundances in Assorted Samples	27
5	Concentrations of RE in Three Sea-Water Fractions	28
6	La Contents and Fractionation Indices of some Sedimentary Materials	57
7	Information on Samples Discussed in 3.3.1	73
C-1	Chemical Yields of Ce <sup>139</sup> and Y <sup>88</sup> in RE Group Separation	159

LIST OF FIGURES

	<u>Page</u>
<u>Fig. 1</u> Chondrite-normalized RE abundances in pelagic red clays and a diatomaceous ooze	37
<u>Fig. 2</u> Chondrite-normalized RE abundances in pelagic brown ("red") clays and in assorted pelagic and non-pelagic marine sediments	39
<u>Fig. 3a</u> Chondrite-normalized RE abundances in an untreated Indian Ocean red clay (V2), in same after "washing" with 0.3% EDTA solution (E2) and in their difference (V2-E2)	42-43
<u>Fig. 3b</u> Chondrite-normalized RE abundances in an untreated Antarctic red clay (V9), in same after "washing" with a 0.3% EDTA solution (E9) and in their difference (V9-E9)	42-43
<u>Fig. 4</u> Chondrite-normalized RE abundances in clay fractions from samples of Equatorial Atlantic globigerina ooze core Al80-74	45
<u>Fig. 5</u> Chondrite-normalized RE abundances in globigerina tests fractions from samples of Equatorial Atlantic core Al80-74	47
<u>Fig. 6</u> Chondrite-normalized RE abundances in Cariaco Trench sediment, Florida Bay calcareous sediment, Black Sea average insoluble sediment and Leavenworth limestone	49
<u>Fig. 7</u> Chondrite-normalized RE abundances in a Bahama oölite, a New Jersey recent shells composite, a Florida Bay Pleistocene coral and upper limits of RE abundances in the acid-soluble part of a recent shell of <u>Polynices Heros</u>	51

	<u>Page</u>
<u>Fig. 8</u> Chondrite-normalized RE abundances in a sword-fish vertebra, in the body of a Quahog clam, and upper limits of RE abundances in the acid-soluble part of a <u>Polynices Heros</u> recent shell	53
<u>Fig. 9</u> Chondrite-normalized RE abundances in four manganese nodules	55
<u>Fig. 10</u> Chondrite-normalized RE abundances in Atlantic sea-water fractions from 1100 m depth and 700 m depth, and in a Pacific unfiltered sea-water from 100 m depth	57
<u>Fig. 11</u> Chondrite-normalized RE abundances in carbonatites from Sangu and Panda Hill (Tanganyika) and from Aln� (Norway)	59

-1-

PART I

RARE EARTH DISTRIBUTIONS  
IN  
THE MARINE ENVIRONMENT

## 1. INTRODUCTION

The distributions of RE in marine materials and sea-water were until very recently completely unknown, and RE data on sedimentary rocks of marine origin (shales, limestones) were scanty. When this program of study was begun in 1962, the only data on a major part of the RE elements were those of Ostroumov (1953), on some sediments from the Black Sea. Total RE concentrations in Indian Ocean sea-water, suspended solids and plankton had been determined colorimetrically by Balashov and Khitrov (1960), and La and Ce had been determined by Goldschmidt (1937) in some Atlantic sea-water. The concentrations of single RE elements, mainly La and Y, had been determined in marine cores by various workers, e.g. Goldberg and Arrhenius (1958).

This survey study has been undertaken to shed some light on this unexplored area, in view of the potential general scientific interest and practical usefulness of knowledge on the geochemical behavior of the RE group in the sedimentary cycle. The general difficulty of fractionation of these elements gives them potential "fingerprinting" value for tracing origins of materials, their extremely low concentrations in sea-water and the resulting short residence time makes them potentially useful in tracing bodies of sea-water, and the variability of the

valency of Ce and Eu, as well as the variability of the relative position of Y in the RE elements series in its behavior in various complexing reactions, make them potentially valuable in tracing the geochemical environments through which a sample with a given RE distribution had passed.

Compared to the variability of RE distributions in igneous rocks, the RE distributions found in some sedimentary sample composites (Minami, 1935) and samples (Haskin and Gehl, 1962; Robinson et al, 1958) were evaluated as rather uniform. This study was intended to find out, among other things, whether uniformity or variability was the rule in various phases and materials in the marine environment. A maximum spread of sample types and locations was therefore selected. The samples are listed and described in Table 1.

During the last three years studies on the complete RE distributions in materials from the marine environment have appeared. The RE distributions in one sample of Pacific seawater, a manganese nodule and a phosphorite were reported by Goldberg et al, (1963), and those in eight marine sediments were reported by Wildeman and Haskin, (1965). Their data are used extensively in the discussions of our results.

Table 1 (continued)  
List of Samples Analyzed

No.	Designation	Full Description	Provenance	Remarks
17	mud	Cariaco Trench Sediment (wet mud, 30% water)	10°40.7'N 65°51.7'W Bottom surface near center of Trench close to steep western slope. Water depth 1317m (Max. depth of trench 1500m) At- lantis cruise #240, core #9, 11/3/57	whole sample
18	Oolite	Bahama oolite	The Great Bahama Bank collected in 1963	whole sample
19	shell	Shell of <u>Polynices Heros</u>	Boston beach, collected in summer 1961	insoluble discarded
20	bone	Hard part ("body") of swordfish vertebra	Atlantic Ocean, caught summer 1964	
21	clam	Body of Quahog clam	Great Harbor, Woods Hole, Mass. off Devil's Food Island. Collected live, June 1964 in 2-3m water depth	
22	nodule	Caryn Peak manganese nodule	Atlantic sea mount Caryn Peak 36°40'N 67°57'W, near deep-sea fan of Hudson submarine canyon	whole sample (section through center)
23	SW	Filtered Atlantic sea- water (0.45µ pore size) from 1100m depth	36°56.5'N 73°09'W. Continental rise off Cape Charles, Va. Crawford cruise #100, sta. 1574, 11/9/63	
24	MPS	Suspended solids >0.45µ filtered out of SW	" " "	
25	Blank of MPS	Millipore filter and re- agents used in obtaining and processing sample MPS		
26	CM	Undialyzable fraction of filtered sea-water (0.45µ pore size) from 700m depth	36°56.5'N 73°09'W. Continental rise off Cape Charles, Va. Crawford cruise #100, sta. 1574, 11/9/63	
27	Carbona- tite	Alnd carbonate	Norway	

Table 1

List of Samples Analyzed

No.	Symbol	Nature of Sample	Depth in core, cm.	Remarks
<u>Red clay core No. V16-75 from Indian Ocean, water depth 4630m; basin S.E. of Mauritius 22°13'S 58°23'E, collected 1/16/60, Lamont collection.</u>				
1	V5	red clay	54-55	Untreated core sample
2	V2	red clay	1224-1225	Untreated core sample
<u>Red clay-diatomaceous ooze core No. V16-132 from Antarctic Ocean, water depth 4590m; Bellingshausen basin (S.E. of tip of S. America), 60°45'S 107°29'W, collected 4/23/60, Lamont collection.</u>				
3	V9	red clay	385-386	Untreated core sample
4	V6	diatomaceous ooze	65-66	Untreated core sample
5	E2	EDTA-treated V2		See 2.1.2 for description of EDTA treatment
6	E9	EDTA-treated V9		
<u>Globigerina ooze core No. A180-74 from Atlantic Ocean, water depth 3330m; Mid-Atlantic Ridge at Equator, Eastern flank, 00°03'N 24°10'W, collected 9/9/52, Lamont collection.</u>				
7	A1	brown clay	97-100	17.6% of core material
8	A2	brown clay	197-200	15.6% of core material
9	A3	brown clay	344-350	10.7% of core material
10	A4	brown clay	401-404	24.5% of core material
11	A1C	globigerina tests >75 $\mu$	97-100	24% of core material
12	A2C	" "	197-200	52% of core material
13	A3C	" "	344-350	36.3% of core material
14	A4C	" "	401-404	23.5% of core material
15	A1K	globigerina tests 25 $\mu$ -75 $\mu$	97-100	7% of core material
16	Blank C	Blank of carbonate samples		

## 2. EXPERIMENTAL

### 2.1 Preparation of Samples for Analysis

#### 2.1.1 Unfractionated Samples

All core samples - "V" group and "A" group - were scraped on all sides with an "X-acto" blade aiming to eliminate all parts that had come in contact with the coring piston and with the saw used to cut the sample section out of the core, then dusted off by a jet of filtered compressed air. The "V" samples were then ground and dried at 110°C. From V5 and V9 small dark granules, presumably manganese nodules, were picked out during grinding and discarded. In V2 the granules were left and ground along with the sample.

All grinding was done manually in a mullite mortar.

The Cariaco Trench sediment was obtained as semi-liquid mud. It was dried in a desiccator (to prevent caking) to a consistency of humid earth, then at 110°C to constant weight, and ground. RE are reported on a dry weight basis.

The oölite grains were washed from the associated seawater until free from soluble salts and adhering clay, then dried at 100°C. Non-spheroid fragments - largely shell debris - were picked out and discarded. After surface leaching proved impractical for RE determination (see 2.2.3) a sample of whole oölite grains

was ground for analysis.

The (frozen) Quahog clam in its intact closed shell was washed with distilled water to free it from clay, blotted and weighed. It was placed in a (weighed) polypropylene beaker and put into an oven at  $\sim 100^{\circ}\text{C}$  where the shell opened in about one hour. It separated readily from the body so that no tissue and very little body-fluid remained on it. The shell was then washed over the beaker, dried and weighed and the wet body weight determined by difference to be 54.0 g. (The shell material, which we intended to analyze for RE in conjunction with the body, was unfortunately lost at a later processing stage).

The sword-fish bone sample was cut out from a fresh vertebra and the softer connective tissue and marrow scraped off as much as possible. It was not dried, so that the RE are reported on the live weight basis.

To sample the manganese nodule a quarter inch thick slice was sawed out across the center of the (spheroidal) nodule, including the very thin siliceous interlayers and its nucleus, possibly a shark's tooth. The whole slice was powdered and mixed as well as possible.

2.1.2 Fractionation of core, shell and sea water samples for  
RE analysis of distinct constituents.

A1C-A4C, A1K. From each of four whole-core samples of the globigerina ooze core Al80-74 the coarse  $\geq 75\mu$  tests were separated out by wet-sieving with distilled water (which should have minimum chemical effect on the various core components beside leaching of soluble salts) and labelled A1C (1 for 1 m depth in the core, C for carbonate) through A4C. From the core section at 1 m the 25-75 $\mu$  carbonate tests fraction and from that at 3.5 m the 35-75 $\mu$  fraction were also separated out for wet-sieving and labelled A1K and A3K, respectively. Both were examined paleontologically (as well as A1C to A4C) but only A1K was analyzed for RE. Each test fraction was further cleaned from adhering clay by repeated ultrasonic shaking with distilled water and decantation, then sieving again. Finally they were blotted, dried and ground.

All sieves were especially prepared by us from white nylon mesh heat-welded onto polyethylene frames.

A1-A4. The remaining  $< 75\mu$ ,  $< 25\mu$  and  $< 35\mu$  fractions consisted mainly of smaller carbonate tests and test debris, an alumino-silicate phase (mainly clay according to Broecker (1958) and referred to further as "clay," for convenience), and possibly some other minor unidentified phases. From this material it was desired to separate out the clay fraction as intact as possible

and with least possible contamination by RE from the other phases present. Dissolution of the carbonate without attack of the clay was attained by using an automatic titrator (by Radiometer) set to pH 4. The solvent was  $\sim 1N$  HCl. Radioactive tracer experiments using carrier-free  $Y^{88}$  were carried out to obtain information on the extent and rate of RE sorption by the clay under these conditions, and on the possibilities of their desorption or prevention of sorption, by EDTA. A preliminary dissolution-run of an amount of the  $<25\mu$  fraction was made using the Radiometer automatic titrator to avoid acidification below pH 4, and when the carbonate was dissolved some Y-tracer was added with stirring, then the insoluble part was separated by centrifugation. It was found to contain more than 70% of the activity. It was deduced that an even higher percentage would have been adsorbed on the clay if the tracer had been added at the beginning of dissolution. It was thus certain, however, that at least 70% of the RE contained in the soluble phase would adhere to the clay under these conditions. In a further experiment the tracer was added to some quantity of the  $<25\mu$  fraction before beginning the dissolution, followed by 5 ml 1% EDTA, then the titration-dissolution was carried out. The final concentration of EDTA in the solution was  $<0.2\%$ , and the centrifuged clay contained only  $<2\%$  of the added tracer. Since carbonates were known to contain

only about one tenth as much RE as clay this procedure, i.e. dissolution at  $\text{pH} \geq 4$  in the presence of enough 1% EDTA to give a final concentration of  $<0.2$  to  $0.3\%$ , was followed to free the clay fraction from the fine carbonate. The centrifuged clay was resuspended twice in  $\text{H}_2\text{O}$  to wash out the excess Ca, Cl and other dissolved ions as well as the EDTA, centrifuged, dried at  $110^\circ\text{C}$  and ground. The four fractions thus obtained were labelled A1 through A4, 1 to 4 again indicating the depth in the core in meters.

E2, E9. It was also established that a 1% solution of EDTA will strip sorbed Y tracer from clay. The tracer was added to and stirred for 10 minutes with suspended clay which was then centrifuged. It was resuspended repeatedly in 5 ml portions of 1% EDTA and stirred each time 5-10 min. with the following results: after one wash  $\sim 8\%$  of the originally adsorbed activity remained, after the second  $3.5\%$ . Two more washings reduced the sorbed activity to  $<2\%$  of the initial.

On the basis of this information stripping of the sorbed RE from samples V2 and V9 by EDTA was attempted. About 2 g of V9 clay and  $<1\text{g}$  of V2 clay were stirred for half an hour each (at room temperature) with 20 ml of  $0.5\%$  EDTA, centrifuged, resuspended and treated the same way a second time. The supernatants were discarded and the solids were dried at  $110^\circ\text{C}$  and ground. The super-

natant of V9 was purple-brown, that of V2 was colorless. The nature of the colored species was not determined; a thiocyanate test showed much  $\text{Fe}^{+3}$ . The EDTA-washed sample of V2 was labelled E2, that of V9 was labelled E9.

Acid-soluble part of Polynices Heros shell. The shell was washed with  $\text{H}_2\text{O}$ , then immersed briefly in 2N HCl to remove the pigmented organic coating of the shell and any adhering extraneous material. The cleaned shell was then washed, dried and weighed (15.75 g), and dissolved in HCl starting with 50 ml of 2N and adding 6N as needed to complete the dissolution. The undissolved organic shell-framework was filtered out on Whatman 42 filter-paper pre-washed with hot 2N HCl. This solution thus included, beside the mineral-part of the shell, only readily soluble organic material which is a very small part, if any, of the total organic material in the shell.

Filtered sea-water and the suspended solids filtered out of it. The 5 liter sample was aspirated from a 200 l. Bowen sampler through a  $0.45\mu$  (HA) Millipore (=MP) filter enclosed in a polystyrene filter holder into a 2 gallon (acid washed) polyethylene bottle, and 50 ml of 2.5N HCl were added to it to bring the pH to about 2 and thus prevent bacterial and mold growth and sorption phenomena. This was done on board, soon after hoisting

up the Bowen sampler. The filter holder-container was designed by the Millipore company expressly for exclusion of contamination from filters and the material retained on them both during the filtration procedure and during storage.

The undialyzable fraction of filtered sea-water. The procedure designed to obtain this fraction was aimed at retaining a maximum of the organic material dissolved in sea-water, which should presumably include a considerable amount of metal-organic complexes, and exclusion of most of the inorganic dissolved RE species. The 5 liter sea-water samples earmarked for this work were therefore aspirated (thru a filter as above) from the same Bowen sampler into (acid-washed) glass bottles, and a low-boiling organic antibacterial preservative was added. Polyethylene bottles couldn't be used since some organic material is known to get leached out of them in time, and acidification was avoided since it might denature proteinaceous materials and cause de-complexation. The preservative was 50 ml (per 5 lit.) of trifluorotoluene, chlorobutane, 1,2-dichloroethane (2:1:1) (after Provasoli). Any organic material that would adhere to the glass during storage can be shaken off by ultrasonics.

The elimination of the bulk of salt and other small ionic and molecular species including the ionic RE was accomplished by

dialysis and flash evaporation. A preliminary experiment with carrier-free  $Y^{88}$  radioactive tracer indicated that the RE dialyzed out of sea-water in straight proportion with chloride ion, and that less than 1% of the total ionic RE was sorbed by the dialysis membrane. In another tracer experiment sorbed ionic RE were found removable from the glass walls of the container by 15 min. of ultrasonic treatment.

The procedure of sample treatment was as follows: removal of preservative by vacuum at room temperature; ultrasonic release of adsorbed substances from walls of sample container at 300 watt power level; dialysis for 24 hours to salinity of 5% through 1" dia. x 12" Visking cellulose dialysis tubing (pre-soaked for 24 hours in 1N HCl) vs. distilled water flowing at 2 ml/min.; repeated ultrasonic cleaning as before; flash evaporation to 1.5 - 2 lit. at 40-50°C using a continuous feed polyethylene tube for transfer from sample container to flash-evaporation flask; resumption of dialysis in that flask (through membrane used before) to salinity of 4.8%; flash-evaporation to 1 lit. (cloudiness of coagulating organic matter appeared at this point); dialysis to salinity 6.1%, ultrasonic removal of possibly adsorbed substances from walls back into solution; flash-evaporation to 350-400 ml (organic matter coagulated here to yellowish solid pieces, up to 1 mm in size, that floated on the surface);

dialysis to 1.3% salinity; evaporation to 100 ml, ultrasonic shaking and transfer to platinum dish and into oven at 90°C for drying. This dried material was labelled OM (for organic molecules) and analyzed for RE. Total salt left as fraction of initial:

$$\frac{1.3}{34.5} \times \frac{400}{5,000} = \sim \frac{1}{340} = \sim 0.3\%$$

Five 2 ml samples were taken for the salinity determination. All HCl used was vycor distilled; all glassware was pre-soaked in hot vycor-distilled HCl and polyethylene washed with it.

## 2.2 Analytical Procedures

A procedure for determination of all RE (including Y) except Gd and Er was developed by the author, in collaboration with D.G. Towell and J. W. Winchester, as the first part of this thesis research program (Volfovsky, Towell and Winchester, manuscript in preparation) and was described in detail in Towell's Ph.D. dissertation (1963). It consists of group separation of the RE from samples (as in the rest of the paper, "RE" will be used as meaning "rare earths and yttrium"), their neutron activation in solution by thermal neutrons along with a standard RE solution, and carrier-free partition chromatography. The methods used for sample "opening" and RE group separation vary according to the nature of the sample and will be

outlined briefly below. The RE chromatography and counting were identical for all samples, modified only slightly after Winchester (1963) and will not be described here. Carrier-free  $\text{Ce}^{139}$  and  $\text{Y}^{88}$  were added to each sample as the first step in all the procedures, for chemical yield determination.

2.2.1 Sample "opening" and RE group separation, procedure A  
(silicates).

Samples with a considerable silicate content were dissolved and fumed with  $\text{HF} + \text{HClO}_4$ , then dissolved in  $\text{HCl}$ . Double ammonia precipitation of  $\text{Fe} + \text{Al}$  (present in all silicates) coprecipitated the RE group and separated it from the bulk of elements soluble in ammonia, and separation of the RE from the other elements in the precipitate by cation exchange column chromatography followed. The RE chlorides were converted to nitrates by fuming with concentrated nitric acid, and a final solution of pure RE in 1 ml dilute nitric acid was gamma counted for  $\text{Ce}^{139}$  and  $\text{Y}^{88}$  utilizing their different gamma radiation energies and compared to standards for chemical yield determination. A part of this solution was irradiated along with a standard RE solution by thermal neutrons at the M.I.T. Nuclear Reactor, aliquots of sample and standard were chromatographed to separate the RE and all eluted fractions were counted, part directly in solution with

a TMC 400 channel analyzer utilizing energy differences of different elements, part in dried (thin source) form by a proportional beta counter.

This procedure was followed for samples V5, V2, V9, V6, E2, E9, A1 to A4, and the Cariaco Trench sediment. The Trench sediment was irradiated 1 hour, all the others 2 hours.

#### 2.2.2 Procedure B (carbonates)

Carbonates contain only traces of elements precipitable by ammonia, so that coprecipitation of the RE on added iron suffices to separate them from practically all elements (except the iron) and cation exchange chromatography is omitted to save time and to avoid the larger volume of acid eluent, thus reducing the possible contamination by RE from reagents (i.e. blank values).

To the HCl solution of carbonates 5 mg of "spec-pure" iron, additionally purified by anion exchange chromatography was added (in solution) and precipitated twice with ammonia. The precipitate was dissolved in 1 ml nitric acid and irradiated. The RE were separated from the iron after irradiation by retaining the latter on a small anion exchange column, and chromatographed etc. as in procedure A.

2.2.3 Modified sample dissolution or RE group separation procedures.

AlC - A4C, AlK. In the dissolution of these samples the objective was to determine only the RE in the tests, and reduce as far as possible any contamination by RE from the small amount of clay that remained with them in spite of the wet sieving, ultrasonic agitation and multiple rinsing. The ground samples (3.8 g A3C, < 1 g AlK, 3 g each of the others) were dissolved by ~ 1.2N HCl keeping the pH at ~ 4 by means of the Radiometer automatic titrator. At the end of this "titration" which took  $\frac{1}{2}$  to 1 hour a small amount of acid was added to reach pH 2 and thus reduce the loss of RE by adsorption to the clay. After 5 min. at pH 2 the solution was centrifuged off and in three samples (A2C, A4C and AlK) out of the five the insoluble part was re-suspended in water, recentrifuged, dried at 105°C and weighed. This dried insoluble part consisting of partly dehydrated clay plus, possibly, some organic insoluble material, was 4.0% of the original sample weight in all three samples. It was hence assumed that in the two others, AlC and A3C, the same percentage was insoluble.

The short duration of contact of the clays with the tests solution at pH 2 at room temperature was expected to practically preclude any attack on the subsurface layers of atoms in the

clay, and freshly adsorbed ions can be expected to desorb more readily than those embedded in the clay surface for geologic time periods. It seems, therefore, that contamination by RE from the clays was indeed rather negligible.

The solutions were analyzed for RE following procedure B. Cerium and yttrium tracer yields were comparable in each sample but ranged from 49% to 84.5% in different samples. A1C and A3C were irradiated for 12 hours, and the other three samples were irradiated for 3 hours.

Oolite. The bulk of the oolite (2 g sample) was dissolved in HCl which was subsequently evaporated and the organic material, a visibly appreciable part of which was insoluble (see p112 for evidence on presence of soluble organic material), was destroyed by repeated fuming with 70% HClO<sub>4</sub>. Continued by procedure B; irradiated for 3 hours.

Polynices Heros shell and carbonatite. To the hydrochloric acid solutions of the shell (see 2.1.2) and of the carbonatite 5 mg of AR iron in solution were added and precipitated with ammonia to coprecipitate the RE group (as in procedure B, except for the lesser purity of the iron used for these two samples). The RE group was isolated from the dissolved precipitate by cation-exchange and the processing was continued according to procedure A,

but a smaller column than needed for silicates was used and correspondingly smaller volumes of HCl eluent, to reduce elution time and blank values. (Procedure B could not be followed throughout because of the unavailability of purer iron at that time.)

Clam. The complete body of the clam was dried to constant weight (6.37 g) and wet-ashed by concentrated  $\text{HNO}_3$  followed by 70%  $\text{HClO}_4$ . Iron addition and precipitation to collect the RE as in procedure B was followed by cation exchange chromatography through a small column as above, needed because of the presence of a considerable amount of phosphate. Iron was then added again and continued as in procedure B.

Sword-fish bone. The ~1 g sample was not dried. The organic material was digested partly in redistilled hydrogen peroxide which disintegrated the bone but didn't visibly affect the small amount of marrow or fat that turned out to be present, and the rest by fuming with 70% perchloric acid. The rest of the procedure was identical to that used for the clam.

Manganese nodule. The bulk of the 0.1 g sample was dissolved in AR 2 N HCl and the siliceous residue in AR HF +  $\text{HClO}_4$ . Continued by procedure A.

Sea-water. The sample, at pH 2, was heated to 90°C in the bottle in which it had been stored, then a solution containing 25 mg of the purified iron used in procedure B ("spec-pure", additionally purified by anion exchange) and the usual tracers were added and mixed in by shaking and continuation of heating. Precipitation with ammonia was followed by prolonged coagulation and settling periods, then the supernatant was syphoned off and filtered through a 0.1 $\mu$  Millipore filter. (Extremely little material - probably less than 1 mg was retained on the filter; it was insoluble in 0.5N warm HCl. It was not included in the analysis to avoid increase of the blank by RE possibly contained in the filter, but its existence should be kept in mind). The centrifuged main precipitate was fumed with HF + HClO<sub>4</sub> to dissolve any <0.45 $\mu$  silicate particles, dissolved in HCl and reprecipitated with ammonium carbonate to leave uranium in solution. (This seems to have eliminated up to 3/4 of the sea-water uranium, but it was inadequate - see discussion.) The precipitate was dissolved in 1.2 ml dilute nitric acid and an aliquot irradiated for 12 hours. The chemical yields were 80% Ce and 88% Y ( $\pm$  3% each).

Suspended solids (MPS) and a blank containing a Millipore filter were ashed in Vycor crucibles in a muffle furnace, then transferred to platinum dishes for treatment with 1 ml each of

HF + HClO<sub>4</sub>. The considerable amounts of tracers that remained in the crucibles after removal of the ashes of the sample and blank were desorbed by heating with 2N HCl and added to the main respective solutions. Continued by procedure B except for one precipitation with ammonium carbonate aiming to eliminate or reduce the content of uranium if any present. Irradiated along with the sea-water RE for 12 hours. Individual RE separated on same DEP column as the sea water.

Undialyzable fraction of sea-water (OM). The organic material in the <2g salt + organic solid residue of the preliminary treatment (2.1.2) was destroyed by repeated fuming with HClO<sub>4</sub>. Continued according to procedure B with three ammonia precipitations. Irradiated along with the two preceding samples (12 hours) and chromatographed on same column.

Reagents used: HF was of AR quality; all other acids and water used in analyses of non-silicate materials were AR and redistilled using a Vycor condenser, unless otherwise stated. Ammonia and ammonium carbonate were prepared by saturating Vycor-redistilled water with the appropriate gases. The iron solution was purified as described in procedure B. The Ce and Y tracers were analyzed and found to be carrier-free as well as free of any contamination by other RE. The RE used for standards were of

-21-

99.9% or 99.99% purity according to the manufacturer (Lindsay Co.).  
The La standard was analyzed and no non-La activity was detectible.

### 3. RESULTS AND DISCUSSION

#### 3.1.1 Analytical Results

The analytical results are presented in Tables 2 through 5. The limits of error of each value are usually based on one standard deviation each of counting statistics on the sum of the gross counts of all fractions containing the element and on the sum of their background counts. When the elution curve (count vs. fraction) indicated tailing from a preceding element the tail was considered as part of a higher "background" the magnitude of which was determined visually by inspection of the elution curve. In such cases the uncertainty range of this assigned "background" was combined with the standard deviation of the gross total count. The same procedure was used on the standards irradiated and chromatographed along with the samples, and each error given in the Tables is combined from the errors of the sample and standard for each element. Large errors thus stem from low total activity of the element in the sample and/or appreciable tailing of a preceding element during RE chromatography of the sample and/or of the standard.

The errors are given in percentages of the absolute values to give prominence to the relative reliability of the various values. An additional tentative criterion of reliability

Table 2

Rare earth abundances in red clays, in diatomaceous ooze,  
in products of EDTA-treatment of red clays, and in the  
average of 17 chondrites

Ele- ment	V5		V2		V6		V9		E2	
	ppm	±%*	ppm	±%*	ppm	±%*	ppm	±%*	ppm	±%*
La	63.0	1%	63.0	1%	18.9	5%	48.5	1%	24.7	0.5%
Ce	114	25%	112	30%	38	25%	103	30%	108	15%
Pr	16.2	12.5%	9.6	25%			10	35%	13	35%
Nd	65	18%	55	50%			37	60%	25.9	12%
Sm	15.5	1%	15.4	1%	3.0	20%	12.2	1%	4.0	15%
Eu	4.14	0.6%	4.01	0.8%	0.588	1%	2.68	0.8%	1.20	1%
Tb	2.38	9%	2.13	15%	0.35	40%	1.50	15%	0.58	12%
Dy	14.1	1%			2.05	10%			3.04	1%
Ho	2.83	6%	2.79	7%	0.52	25%	1.98	7%	0.53	5%
Tm	1.10	3%	1.40	35%	0.18	5%			0.18	8%
Yb	7.06	7%	6.46	10%	1.07	10%	5.2	10%	1.46	7%
Lu	1.02	8%	1.2	17%	0.136	12%	1.02	14%	0.20	7%
Y	69.4	5%			11.2	15%			12.5	4%

\* Estimated error percentage

- (1) Blank values for silicates taken from Volfovsky et al. in Towell (1963)
- (2) Average of 17 chondrites taken from Schmitt et al. (1964)
- (3) About 5% missing
- (4) 2% - 3% missing
- (5) Difference between the listed Pr values of V2 and E2 is negative. 1.9 ppm is the difference between the upper limit of error of V2 and the lower limit of error of E9
- (6) b.l. = below limit of detection

Table 2 (continued)

Rare earth abundances in red clays, in diatomaceous ooze,  
in products of EDTA-treatment of red clays, and in the  
average of 17 chondrites

E9		V2 - E2		V9 - E9		Blank <sup>(1)</sup>	17 chond- rites <sup>(2)</sup>
ppm	±%*	ppm	±%*	ppm	±%*		ppm
13.5	0.5%	38.3	1%	35.0	1%	0.23	0.30
52.6	10%	4	100%	50	60%	0.1	0.84
5.36	14%	1.9 <sup>(5)</sup>	100%	4.7	80%	0.06	0.123
13.8	8.6%	29	100%	23	100%	0.46	0.564
3.62	1%	11.4	6%	8.6	2%	0.007	0.198
0.704 <sup>(3)</sup>		2.80	1%	1.97 <sup>(4)</sup>	1%	0.0015	0.072
0.53	14%	1.55	20%	0.97	25%	0.006	0.048
2.96	1%					0.0075	0.297
0.53	5%	2.26	9%	1.45	10%	0.0016	0.072
0.222	6%	1.2	45%			b.l. <sup>(6)</sup>	0.031
1.64	7%	5.0	12%	3.57	15%	b.l.	0.17
0.237	7%	1.0	20%	0.79	20%	b.l.	0.031 <sub>5</sub>
14.0	4%					0.025	1.95

\* Estimated error percentage

(1) Blank values for silicates taken from Volfovsky et al. in  
Towell (1963)

(2) Average of 17 chondrites taken from Schmitt et al. (1964)

(3) About 5% missing

(4) Actually 2% to 3% less

(5) Difference between the listed Pr values of V2 and E2 is negative.  
1.9 ppm is the difference between the upper limit of error of  
V2 and the lower limit of error of E9

(6) b.l. = below limit of detection

Table 3

Rare earth abundances in EDTA-treated clays and  
in globigerina tests from core A180-74

Element	A1 ppm	A1 ±%	A2 ppm	A2 ±%	A3 ppm	A3 ±%	A4 ppm	A4 ±%	An (a) ppm	An (a) ±%	A1C ppm	A1C ±%
La	>2.9		>3.5		31.2	2%	46.1	5%	39.2	16%	4.30	3%
Ce	>15.6		69-80	26%	75	25%	76	25%	75.9	25%	6.8	30%
Pr			8.0	15%	8.31	11%	9.2	25%	8.53	8%	1.22	15%
Nd			49(f)	25%	30	17%	27.3	13%	28.5(g)	5%	3.77	25%
Sm			6.98	1%	5.84	2%	6.70	1%	6.50	11%	0.638	2%
Eu	1.13	10%	1.31	1%	1.24	1%	0.978	1%	1.16	16%	0.145	0.6%
Tb	0.63	15%	0.80	7%	0.59	20%	(h)		0.71	26%	0.111	7%
Dy	3.62	1%	3.55	5%	4.16	10%	3.70	1%	3.75	11%	0.562	7%
Ho	0.87	13%	0.87	5%	0.77	11%	0.672	7%	0.80	15%	>0.060	
Tm	0.38 (i)	10%	0.285	6%	0.398	7%	0.283	5%	0.33	18%	0.0541	4%
Yb	2.15	5%	1.82	10%	2.45	7%	1.75	3%	2.1	22%	0.25	15%
Lu	0.342	3%	0.317	6%	0.41	6%	0.267	5%	0.33	22%	0.0368	6%
Y	22.4	8%	22.6	2%	25.0	7%	28.3	5%	24.5	15%	5.08	10%

\* Estimated error percentage

# Maximum deviation from

average, percentage

(a) Average of A1 to A4

(b) Average of A1C to A4C

(c) Blank of A1C to A4C, for  
about 5 g sample

(d) Just above limit of

detection

(e) Below limit of detection

(f) A radioactive unknown contaminant was present

(g) Excluding A2

(h) 0.65 or 0.89 ppm ( $\pm 25\%$ ). Countings two days apart

(i) Inexplicably gave these divergent values

(j) Standard used to calculate this value was not irradiated  
simultaneously with the sample

Table 3 (continued)

Rare earth abundances in EDTA-treated clays and in globigerina tests from core AL80-74

Element	A2C		A3C		A4C		AnC(b)		AlK		Blank(c)	
	ppm	±%	ppm	±%	ppm	±%	ppm	±%	ppm	±%	μg	±%
La	3.16	1%	3.50	2%	4.08	1%	3.76	15%	>9.1		0.168	3%
Ce	5.7	15%	3.9	30%	5.66	9%	5.5	29%	23.2	10%	0.075(d)	80%
Pr	0.766	7%	1.3	15%	1.08	9%	1.0	26%	3.46	8.5%	<0.005(e)	
Nd	3.40	10%	2.8	25%	4.05	8%	3.5	19%	12.4	6%	<0.023(e)	
Sm	0.580	4%	0.595	6%	0.676	1%	0.625	8%	2.26	1%	0.00043	30%
Eu	0.133	4%	0.177	5.6%	0.155	1%	0.15	15%	0.562	4.5%	0.00014	16%
Tb	0.106	10%	0.124	7%	0.094	18%	0.11	14%	0.405	15%	<0.004(e)	
Dy	0.532	2%	0.666	7%	0.666	2%	0.60	12%	2.27	5.5%	0.0019	18%
Ho	0.126	10%	>0.064		0.12	10%	0.123	10%	0.527	13%	0.0003	16%
Tm	0.0425	6%	0.0576	4%	0.0556	5%	0.051	18%	0.175	15%	0.0016	25%
Yb	0.265	6%	0.28	20%	0.328	5%	0.28	15%	0.88	5%	0.001	20%
Lu	0.042	3%	0.045	10%	0.0437	4%	0.042	12%	0.171	2%	0.00136	15%
Y	3.92	8%	5.40	11%	3.71	5%	4.47	20%	18.3	6%	0.008	15%

\* Estimated error percentage  
 # Maximum deviation from average, percentage  
 (a) Average of A1 to A4  
 (b) Average of A1C to A4C  
 (c) Blank of A1C to A4C, for about 5 g sample  
 (d) Just above limit of detection

(e) Below limit of detection

(f) A radioactive unknown contaminant was present

(g) Excluding A2

(h) 0.65 or 0.89 ppm (± 25%). Countings two days apart inexplicably gave these divergent values

(i) Standard used to calculate this value was not irradiated simultaneously with the sample

Table 4

Rare Earth Abundances in Assorted Samples

Element	1	2	3	4a	4b	5	6	7				
	ppm	±%*	ppm	±%*	ppm	±%*	ppm	±%*				
La	17.6	8%	<0.033	0.0643	9%	0.545	0.057	25%	185	5%	406	1%
Ce	40	26%	(3.05)##	10%	15%	0.928	( $<1.6$ )#		1000	25%	897	5%
Pr	5.6	11%	0.056	20%	12%	0.0960	0.034	100%	32	6%	76.0	5%
Nd	17.6	8%	(0.45)##	35%	17%	0.257	( $<0.33$ )#		132	7%	254	5%
Sm	3.45	5%	0.051	1%	8%	0.058	0.0065	30%	38.0	2%	53.5	**
Eu	0.71	5%	0.014	3%	5%	0.0112	0.00083	25%	9.8	2%	8.67	1%
Tb	0.56	22%	0.015	20%	7%	0.0068	( $<0.024$ )#		6.0	6%	2.93	10%
Dy	2.3	5%	0.073	13%	10%	0.0384	0.003#	60%	27.6	2%	11.4	2%
Ho	0.45	10%	0.023	7%	7%	0.00606	0.0007	100%	5.3	2%	1.70	20%
Tm	0.18	20%	0.0077	14%	25%	0.0014	( $<0.0022$ )#		1.77	12%	0.70	12%
Yb	1.34	10%	0.037	15%	36%	0.0043	0.0022	30%	13.2	15%		
Lu	0.25	20%	0.0065	12%	45%	0.00089	0.001	60%	1.7	10%		
Y	11.2	10%	0.970	2%	6%	0.0247	0.028	60%	80	10%		

\* Estimated error percentage  
 \*\* Error unestimable  
 # Below limit of detection  
 ## The high Ce and Nd are apparently mainly fission products of uranium. See Pp.115-116

1 - Carisco Trench sediment  
 2 - Bahama oolite  
 3 - Shell of Polynices Heros

4a - Quahog clam, wet body  
 4b - " " dried body  
 5 - Bone of swordfish  
 6 - Manganese nodule  
 7 - Alnd carbonatite

Table 5

Concentrations of RE in three Atlantic sea-water fractions and in Pacific unfiltered sea-water

Element	Filtered sea water (sw) ng/l (a)	±% ±*	Suspended solids (MPS) ng/l (a)	±% ±*	Blank of MPS μg#	±% ±*	Undielyzable fraction of filtered sea-water (OM) ng/l (a)	±% ±*	Pacific unfiltered sea-water (g) ng/l (a)
La	62	35%	21.2	5%	0.0130	5%	10.6	+ 14.2 ng/l (f) - 8.4 ng/l	2.9
Ce	(740) (b)	(10%)	13	(h)	0.05 (d)	100%	(570) (b)	(10%)	1.3
Pr	<4.4 (c)	33%	<5 (c)	50%	b.l. (e)		<2.1 (c)	100%	0.64
Nd	(126) (b,c)	(5%)	<30 (c)	10%	b.l. (e)		(<65) (b,c)	(8%)	2.3
Sm	1.36	7%	2.94	2%	0.00085	10%	0.25	20%	0.42
Eu	0.29	10%	0.724	1%	0.00019	5%	0.085	16%	0.114
Tb	0.15	(i)	0.56	28%	0.0008	50%	0.1	35%	
Dy	1.5	30%			0.00157	3%	0.48	37%	0.73
Hg	0.29	20%	0.30	14%	0.0002 (d)	25%	0.10	32%	0.22
Tm	0.25	60%	0.18	80%	0.0002 (d)	100%	0.16	50%	0.13
Yb	1.14	30%	1.0	25%	0.0005	50%	0.47	30%	0.52
Lu	0.13	70%	0.16	20%	0.00022	25%	0.05	90%	0.12
Y	20.4	10%	8.74	13%	0.0085	17%	7.6	15%	

\* Estimated error percentage

# Amount of RE found in reagents and Millipore used in filtering out and analyzing the suspended solids from 5 l. of sea-water

(a) ng/l = nanograms (10<sup>-9</sup>g) per liter

(b) The high Ce and Nd values indicate that they are largely fission products of uranium which was not adequately removed prior to irradiation

(c) The blanks of Pr and Nd were below limit of detection, but not negligible

(d) At limit of detection

(e) b.l. = below limit of detection

(f) Blank very uncertain

(g) 20 l. sample from 100m depth, after Schmitt and Smith, (1962); Goldberg et al., (1963)

(h) Uncertain to a factor of 2

(i) Uncertain to a factor of 3

of results is proposed in the next section.

### 3.1.2 Graphic presentation of RE data

In all the figures our data as well as pertinent data from literature are presented by plotting the ratios of the RE abundances in each sample to the corresponding average RE abundances in 17 chondrites on a logarithmic scale as a function of atomic number. The average chondrite values were taken from Schmitt et al. (1963).

Masuda (1962) and Cooyell et al. (1963) independently observed that RE patterns of samples could be compared and interpreted most readily when instead of their absolute RE abundances ratios of the sample RE abundances to those in the reference material were plotted. This is so because the natural abundance of any RE with an even atomic number is always higher than those of the adjacent RE with odd atomic number, due to nuclear stability differences. Plots of absolute RE abundances thus always have zig-zag patterns which are difficult to compare in detail. They used mainly the chondritic RE averages as a reference and plotted the RE ratios on a logarithmic scale, against the atomic number of the RE.

Since then all results and discussions of RE abundances by authors in this country and in Australia have been presented

using the ratio plotting method either as described above or with modifications (Schmitt et al, Chase et al, Taylor, Haskin and coworkers, Goldberg et al, Towell et al, and most recently Fleischer in an extensive review of existing RE data). The principal modifications were: using the RE radius (after Ahrens, 1952) as the abscissa, instead of the atomic number (Schmitt, Haskin, Goldberg); using the RE average of 7 sediments (Haskin, Goldberg) or the RE values of a North American shale composite (Haskin, more recently as the reference basis for the RE ratios; normalizing all the ratios so that the La ratio = 1.00 (all except Chase) or the Yb ratio = 1.00 (Haskin and coworkers) or the "norm" ratio = 1.00 (Wildeman and Haskin, 1965). Most authors have used a linear rather than a logarithmic scale for the ordinate.

The method of presentation of Coryell et al. (1963) is used here without modifications and is considered preferable for the following reasons:

Atomic number as the abscissa. Appreciably different values of the RE radii have been given by different authors (Goldschmidt, 1926; Ahrens, 1952, Pauling, 1960, based on earlier work; Templeton and Dauben, 1954). They differ in absolute magnitude and, more importantly, in the increments between adjacent elements which vary regularly according to some, notably Templeton

and Dauben, and irregularly according to others, notably Ahrens. All the determinations were made on crystals of pure simple RE compounds. In the complex and crystallochemically widely different structures in which RE occur in nature, mostly as trace impurities, their effective radii are likely to be different and, moreover, to vary from material to material. Furthermore, the larger, lighter RE ions are probably rather easily deformable. Only the inner regularity of the radius decreasing with increasing atomic number, (the "lanthanide contraction") is probably always maintained, and therefore the use of the atomic number for the abscissa follows the general trend of the radii and the ionic potential (proportional to the reciprocal of the radii) of the RE and at the same time stresses the qualitative nature of our knowledge of their exact values. It is noteworthy that in the set of radii given by Templeton and Dauben - the only one in which the third decimal is given and considered significant on a relative scale - the reciprocal values of the radii vary almost exactly linearly with atomic number except for La which lies lower (see plot in Towell et al, 1965). This regularity as well as the greater refinement of their results would seem to render them more plausibly correct than the earlier determinations.

The chondrite RE average as reference set of RE values:

The very narrow range of variation of RE abundances in most of the chondrites analyzed for them, as well as other evidence, has led many authors to consider the chondrites as the best presently available representation of the non-volatile part of the actual primary material of the solar system including the earth, from which the core, mantle and crust of the latter evolved by geochemical differentiation. RE patterns revealing relative enrichment or depletion with respect to such material are geologically meaningful since they reflect geochemical processes of evolution from a parent material to a differentiation or alteration product. The sedimentary crustal average, on the other hand, does not represent any single material but a variety of materials whose individual RE patterns vary considerably (see 3.1.3). Using this average (even when it is adequately determined, which at present it is not) as the reference set of RE values reveals the conformity, or lack of it, of a given sample with the average, but the geochemical evolution of the sample cannot be traced from this comparison since geochemical processes can be inferred mainly from comparison of patterns in actual materials between which some genetic relationship exists.

Use of the chondrite average as reference (referred to further as "chondrite-normalization") results most often in

remarkably smooth patterns which are easy to inter-compare (see Schmitt et al. 1963, 1964; Chase et al., 1963 and this work) and possible genetic relationships between different materials presented in this manner seem easiest to evaluate.

The logarithmic scale. Plotting the RE ratios on a logarithmic scale rather than on a linear one, seems to us most important. The different RE patterns are results of fractionation phenomena, where fractionation factors are of main interest, and only on a logarithmic scale do equal factors between large numbers and small numbers look equal. On a linear scale enrichments are always more prominent than depletions; e.g. selective enrichment of an element by a factor of 3 with respect to the adjacent elements plots 3 times bigger than depletion by the same factor which is geochemically of the same importance. A noteworthy illustration is Goldschmidt's widely accepted and quoted statement that in Minami's shale average and, by inference, in all sediments, Eu is "normal" in contrast to many minerals and most non-basic rocks where it is depleted. Masuda (1962), who plotted the chondrite-normalized values of the same shale average on a logarithmic scale was apparently the first to point out that, in fact, Eu is depleted in it by a factor of almost 2 relative to chondrites and thus also relative to basalts (in which Eu is normal relative to chondrites).

The prominence of differences between large numbers and the de-emphasis of factorially similar differences between small numbers inherent in the linear scale has also led Fleischer (1965) to differ from Frey and Haskin (1963) in the evaluation of the similarity (or lack of it) of the Mohole and Atlantic Ridge basalts' RE pattern to that in chondrites - a key question for the chondritic earth model and the understanding of the formation of the Mid-Atlantic Ridge. The difference stems from normalization of the ratios to La = 1.0 by Fleischer and to Yb = 1.0 by Frey and Haskin. On a logarithmic scale the difference in normalization would have made no difference in the graphic presentation.

(A subsidiary advantage of the logarithmic scale is that mistakes in placement of the decimal point which occur rather often in the normalization calculations, especially where small numbers are involved, and are easily overlooked in plots on a linear scale, draw immediate attention in logarithmic scale plots since they show up as a selective enrichment or depletion by a factor of 10 which occurs in nature very rarely and is always very striking on the log scale.)

Proposal of a graphic criterion of reliability of RE values. Inspection of logarithmic scale plots of chondrite-normalized RE analyses made by different methods and different

analysts has led us to observe that the results of some authors plot rather consistently closer to smooth curves than those of others. Since all chemical properties of the RE vary rather smoothly from element to element and, in particular, never zig-zag, a rather smooth (normalized) variation should be the rule in natural RE fractionations too (except for elements like Ce, Eu, possibly Yb, and Y). Based on these considerations we believe and propose to regard a smooth variation pattern as indicative of a good quality of the analytical data and that, conversely, an irregular zig-zagging (though normalized) pattern should be regarded with caution. Except for Ce, Eu and Y, single points off a generally smooth pattern line should be regarded as likely to be erroneous.

Again, only plots on a logarithmic scale enable one to make full use of this criterion since the heavy RE which are usually depleted with respect to the lighter ones and thus have low chondrite-normalized values often appear to lie on a rather smooth line on a linear plot, especially when the normalization to La = 1.0 is used, even when there is relative bouncing by considerable factors.

According to this criterion RE analyses made by X-ray spectrography and X-ray fluorescence tend to be rather inaccurate except when quite large quantities of pure RE from the sample are available to the analyst, and neutron activation analyses tend to be better.

FIG. 1

Ratios of the RE abundances in pelagic red clays from an Indian Ocean core (V5 and V2) and a pelagic red clay and diatomaceous ooze from an Antarctic Ocean core (V9 and V6) to the corresponding average RE abundances in 17 chondrites plotted on a logarithmic scale as a function of atomic number. (see Table 2)

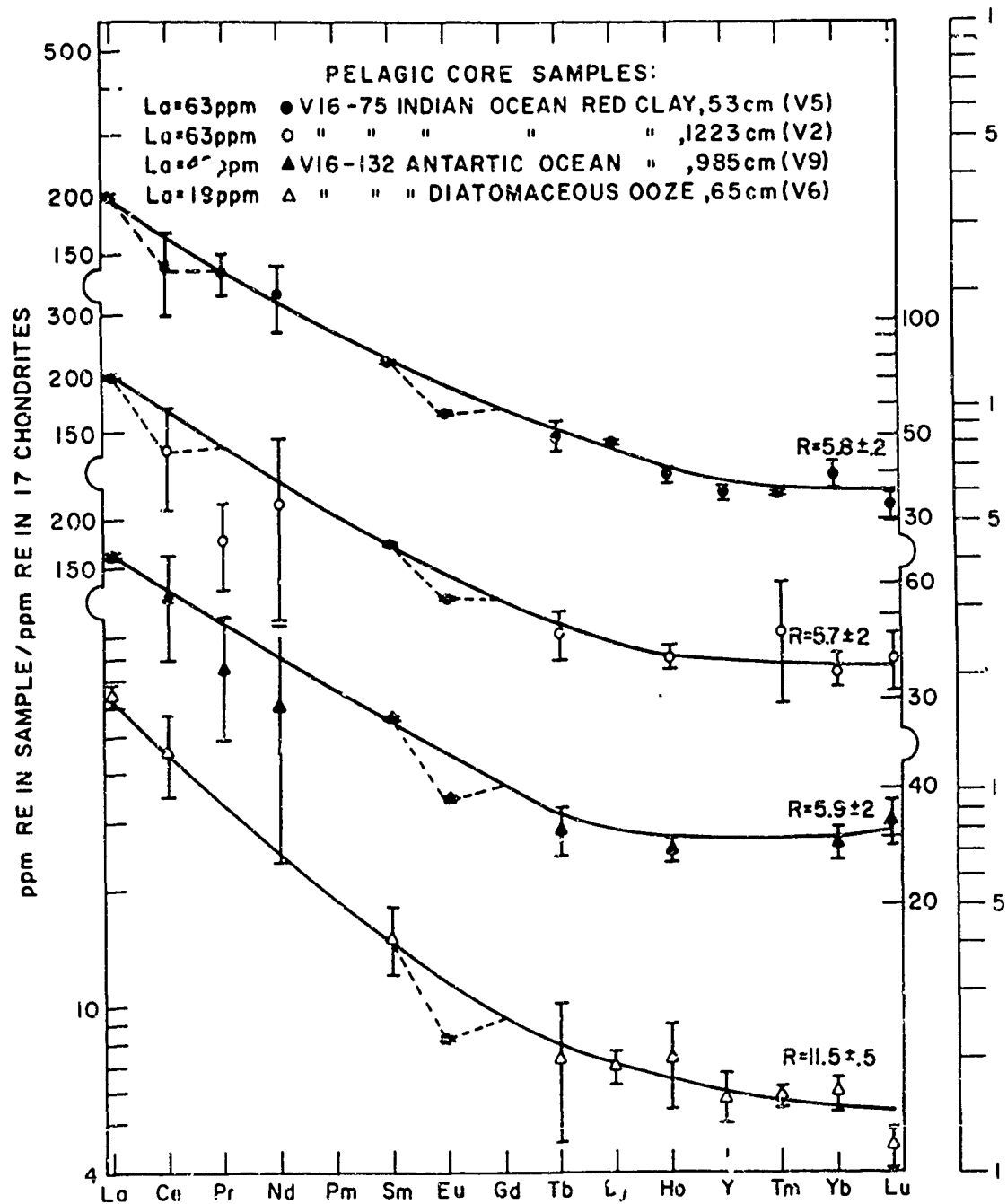


FIG.2

Ratios of the RE abundances in pelagic brown ("red") clays from two Atlantic Ocean cores and in assorted pelagic and non-pelagic marine sediments from the N.E. Pacific, to the corresponding average RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. The data on the phosphorite (bottom curve) are from Goldberg et al. (1963). The rest is from data by Wildeman and Haskin (1965).

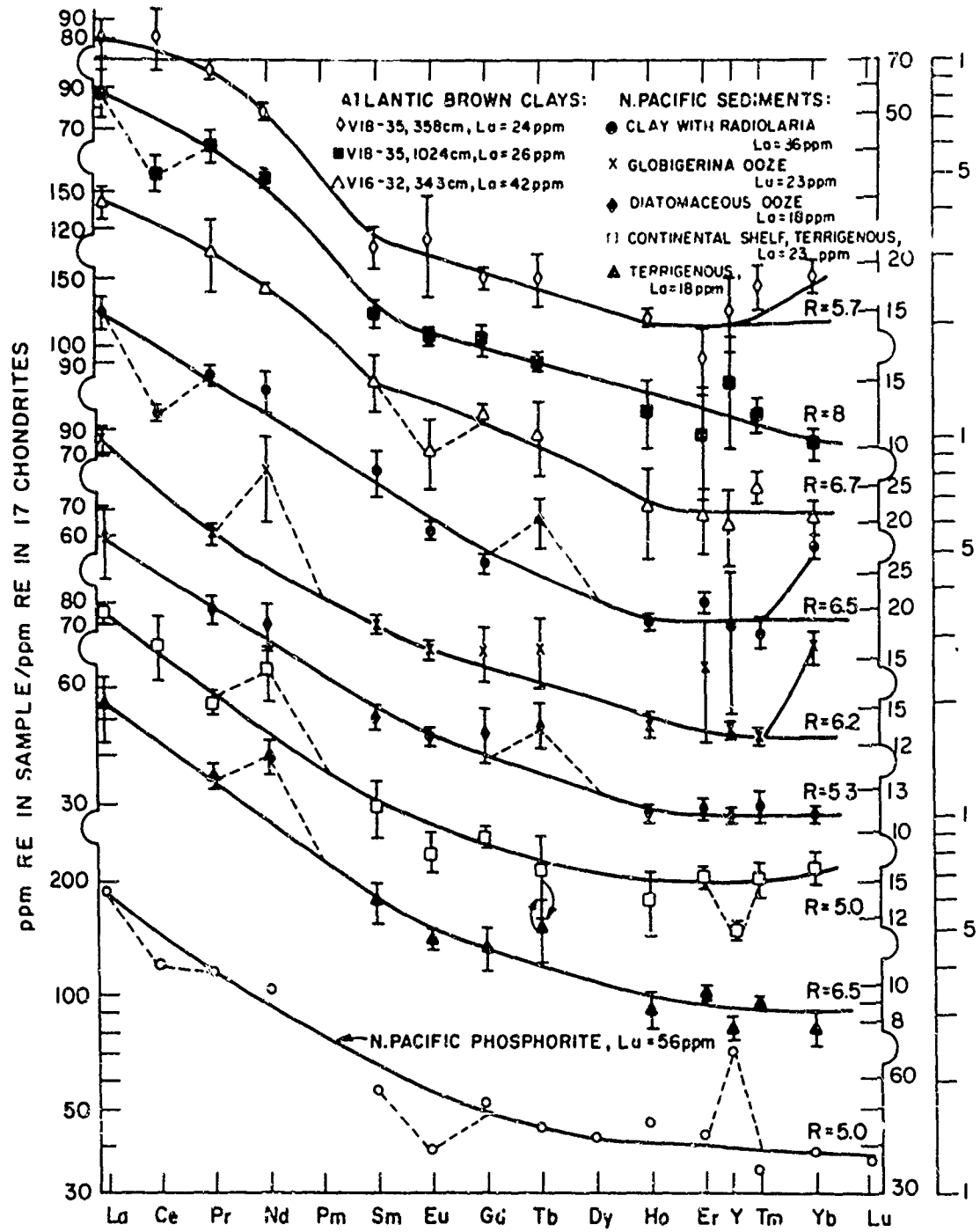


FIG. 3a

Ratios of the RE abundances in an untreated Indian Ocean red clay ( V2 ), in same after "washing" with a 0.3% EDTA solution (E2) and in their difference (V2-E2), to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. (See Table 2)

FIG. 3b

Ratios of RE abundances in an untreated Antarctic red clay (V9), in same after "washing" with a 0.3% EDTA solution (E9) and in their difference (V9-E9), to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. (See Table 2)

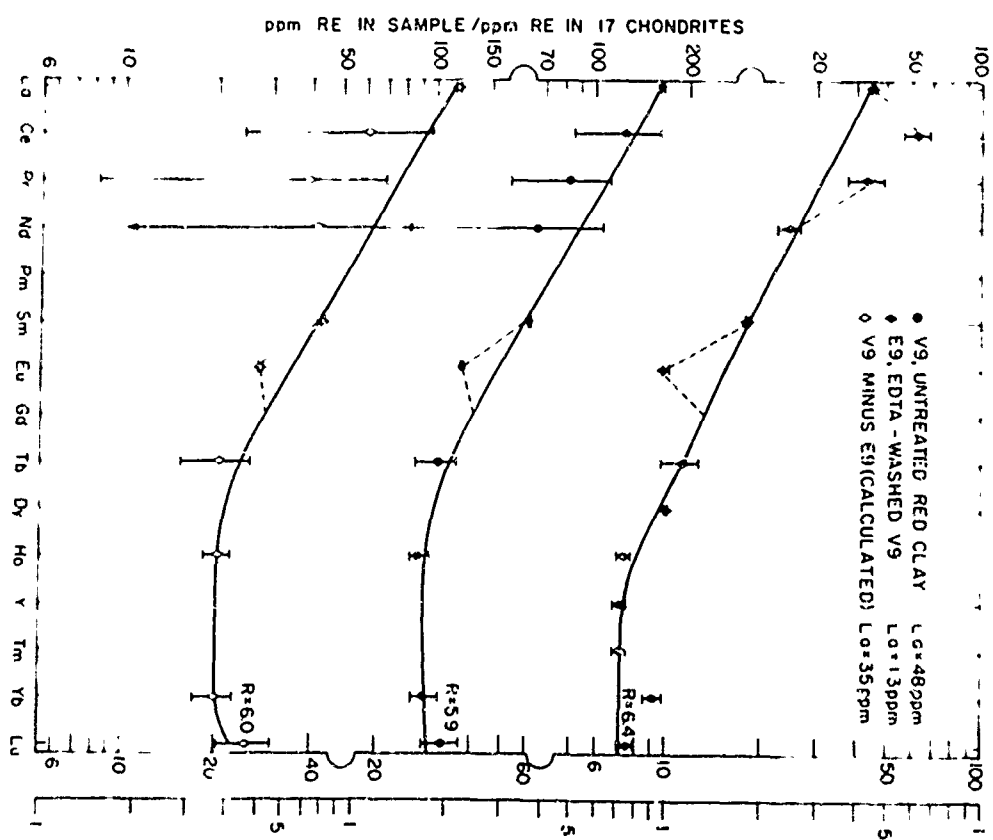
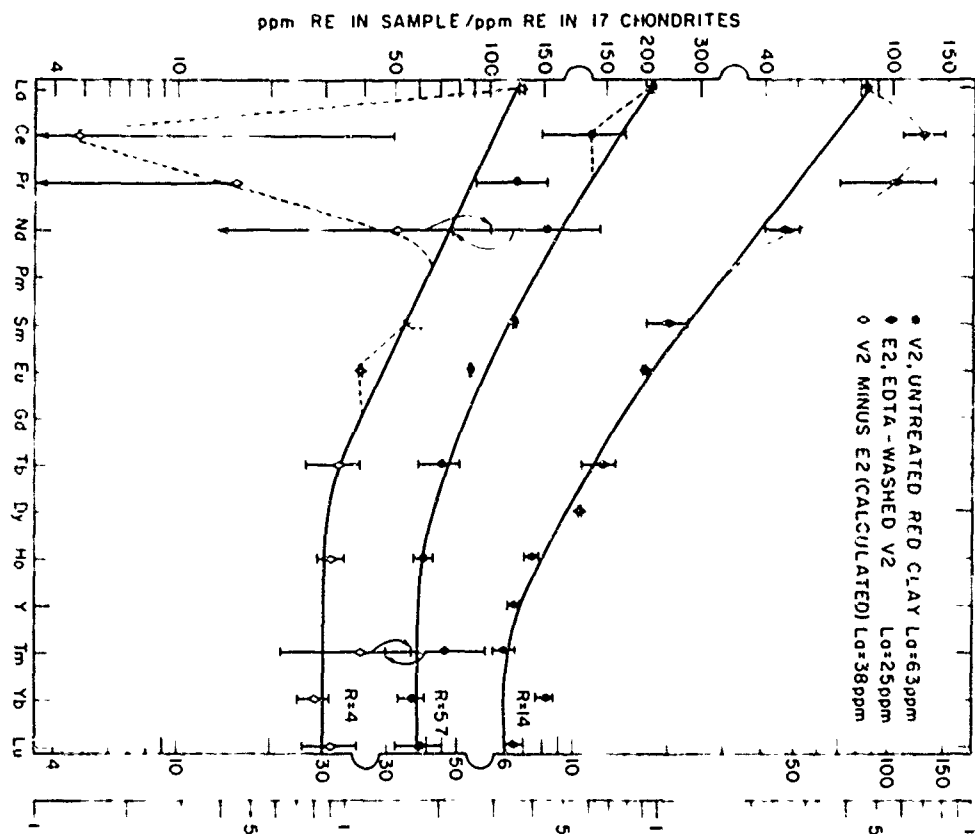


FIG. 4

Ratios of the RE abundances in clay fractions from samples of Equatorial Atlantic globigerina ooze core A180-74, separated from acid-soluble material by dissolving the latter in HCl at pH 4 in the presence of <0.5% EDTA, to the corresponding RE abundances in 17 chondrites plotted on a logarithmic scale as a function of atomic number. (See Table 3)

Also shown is the average shale composite of Haskin and Gehl (1962).

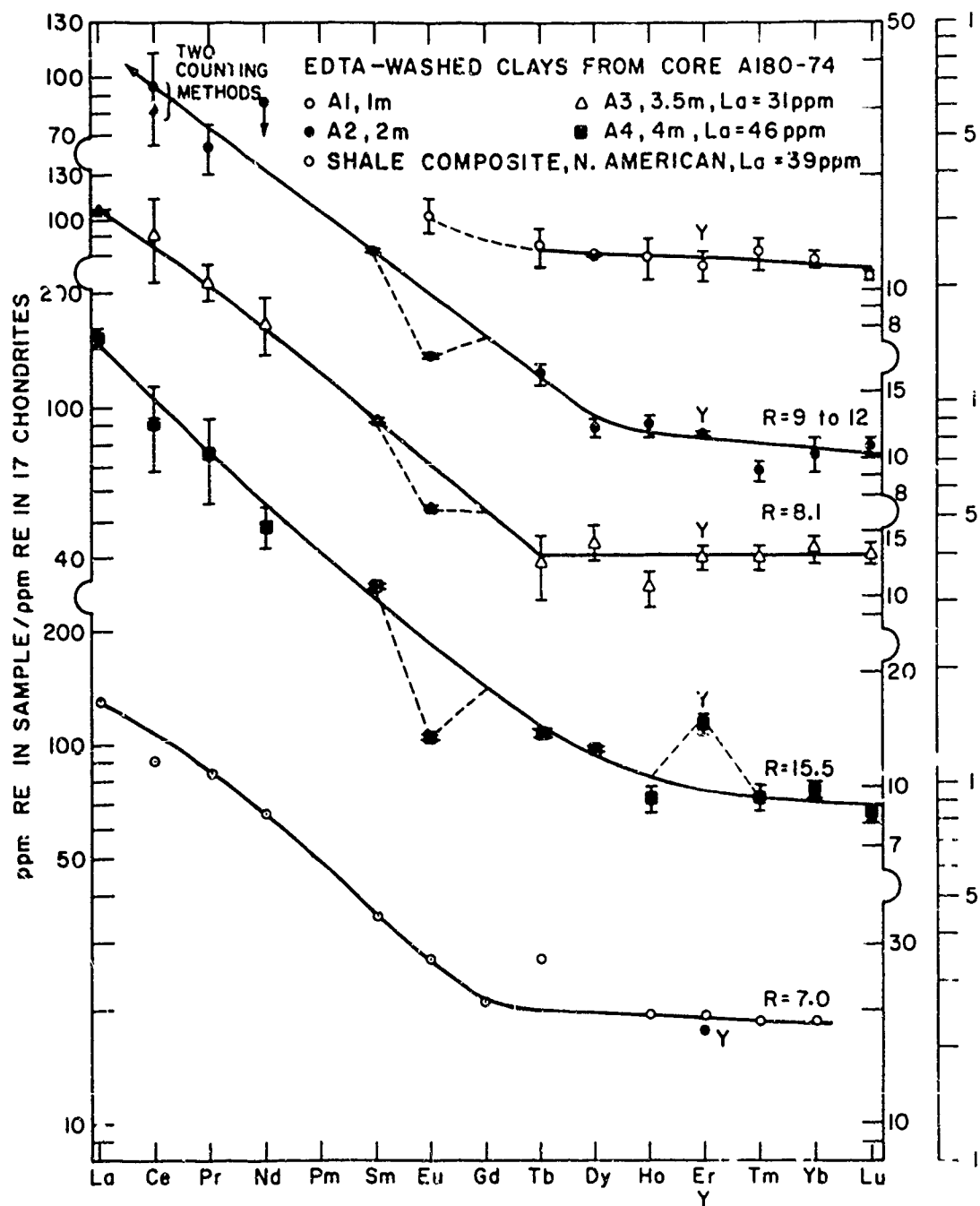


FIG. 5

Ratios of the RE abundances in globigerina tests fractions (25-75 $\mu$  and >75 $\mu$ ) from samples of Equatorial Atlantic core A180-74, separated out by wet sieving, to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. (See Table 3)

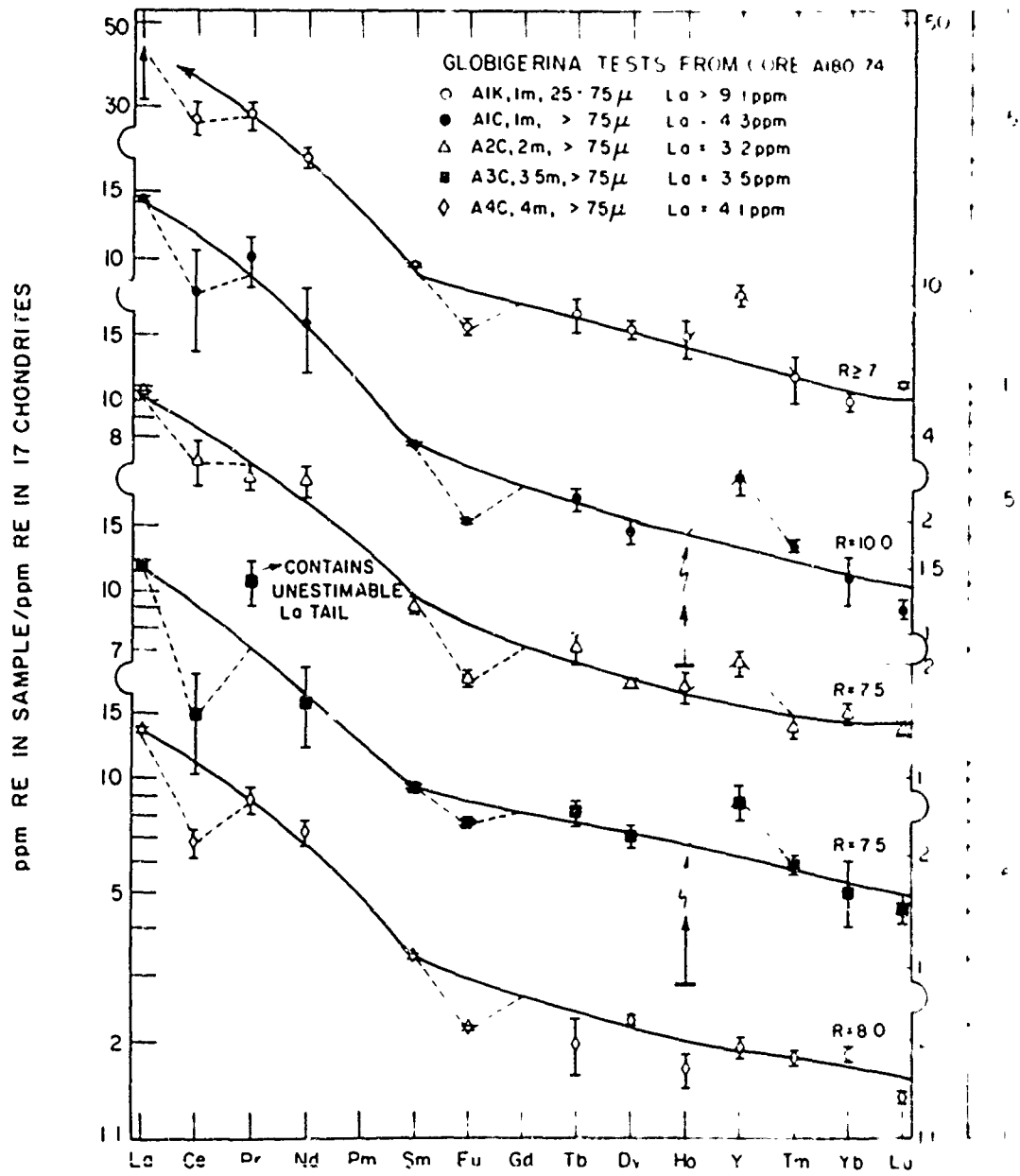


FIG. 6

Ratios of the RE abundances in Cariaco Trench sediment (see Table 4), Florida Bay calcareous sediment, Black Sea average insoluble sediment and Leavenworth limestone, to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. The Black Sea data are from Ostroumov (1953), the Florida Bay sediment and Leavenworth limestone from Haskin and Gehl (1962).

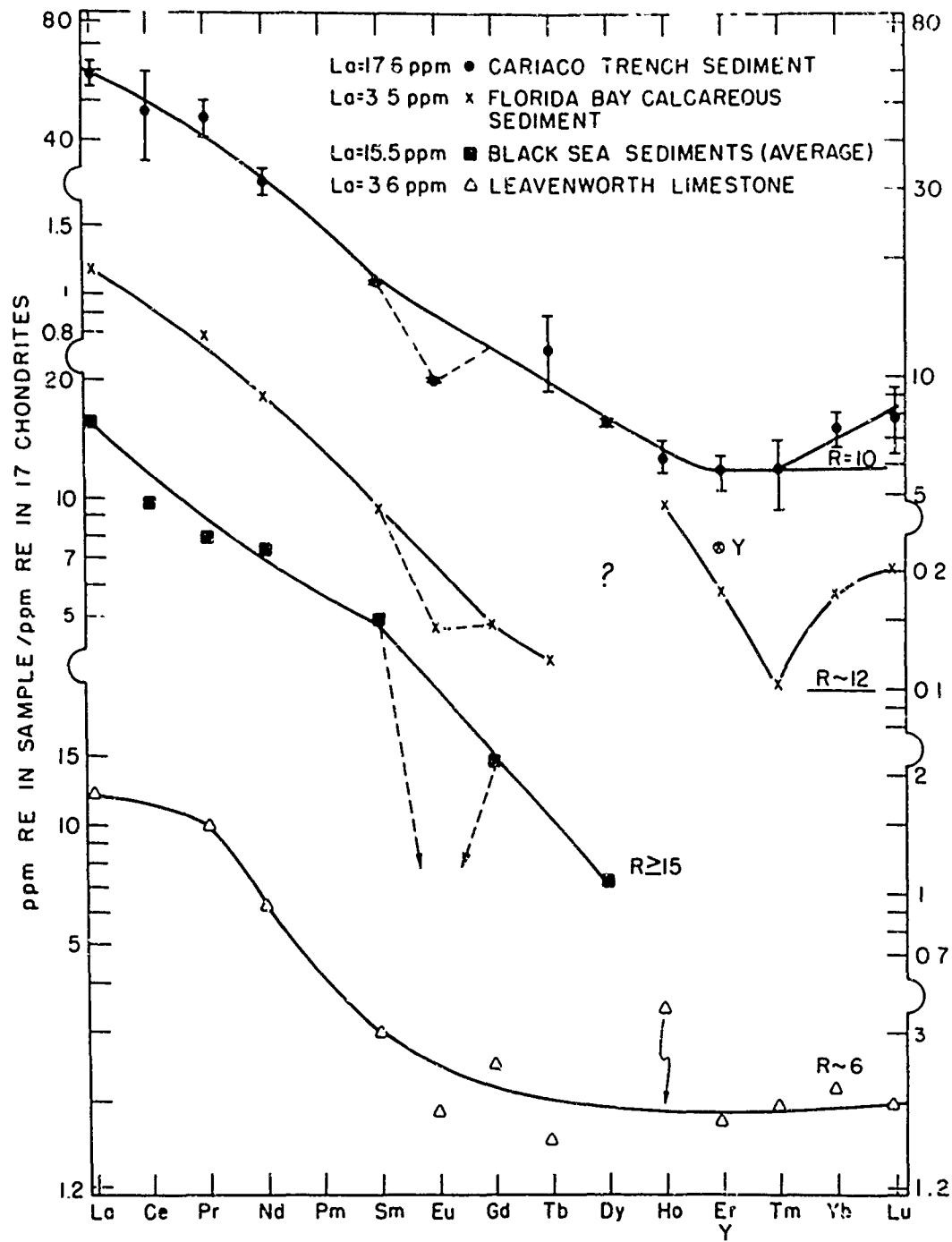


FIG. 7

Ratios of the RE abundances in a Bahama oölite, a New Jersey recent shells composite, a Florida Bay Pleistocene coral and of upper limits of RE abundances in the acid-soluble part of a recent shell of Polynices Heros to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. For oölite and single shell data see Table 4, the others are from Schofield and Haskin (1964).

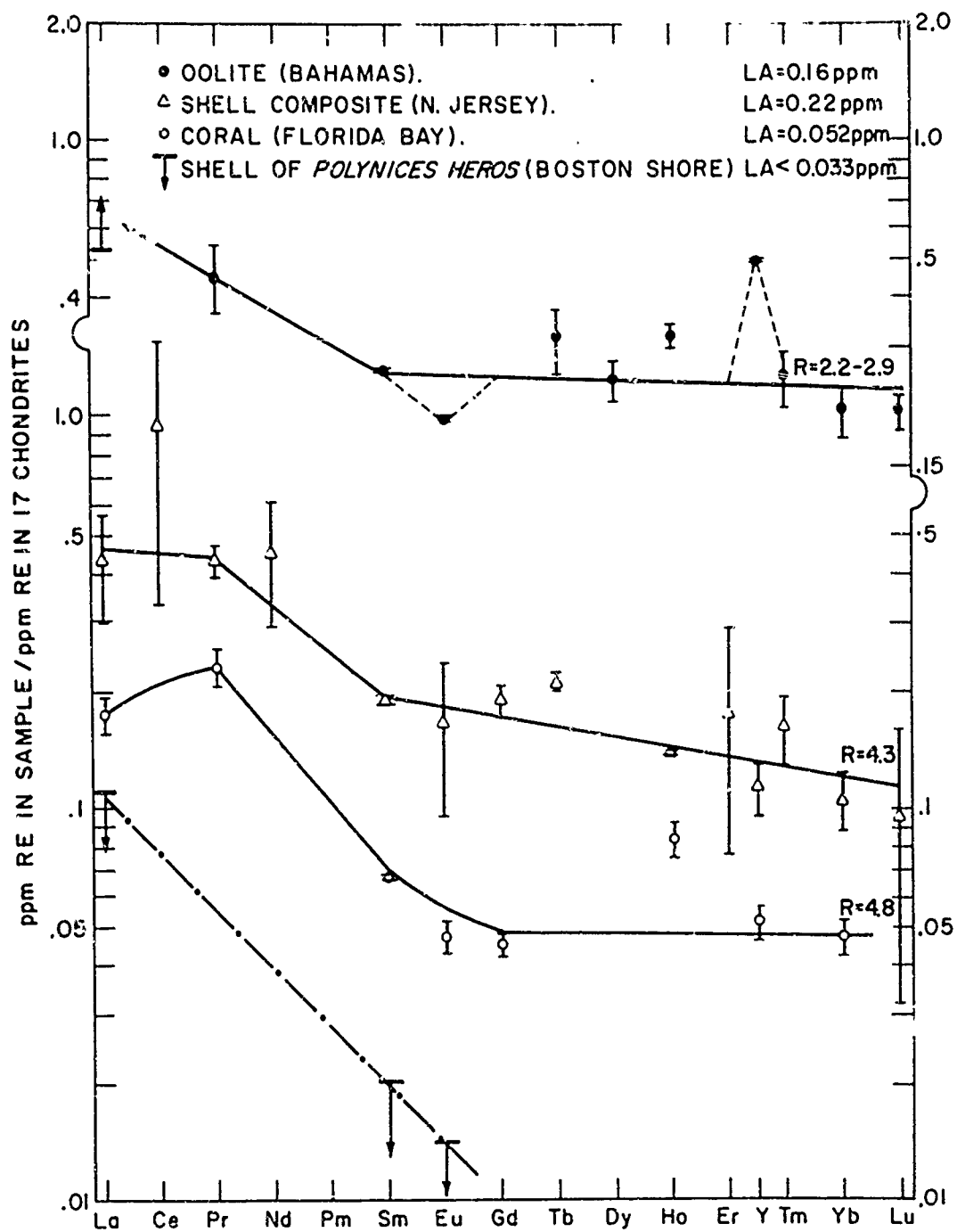


FIG. 8

Ratios of the RE abundances in the body (=bony part) of a sword-fish vertebra, in the body of a Quahog clam and of upper limits of RE abundances in the acid-soluble part of a Polynices Heros recent shell, to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. (See Table 4)

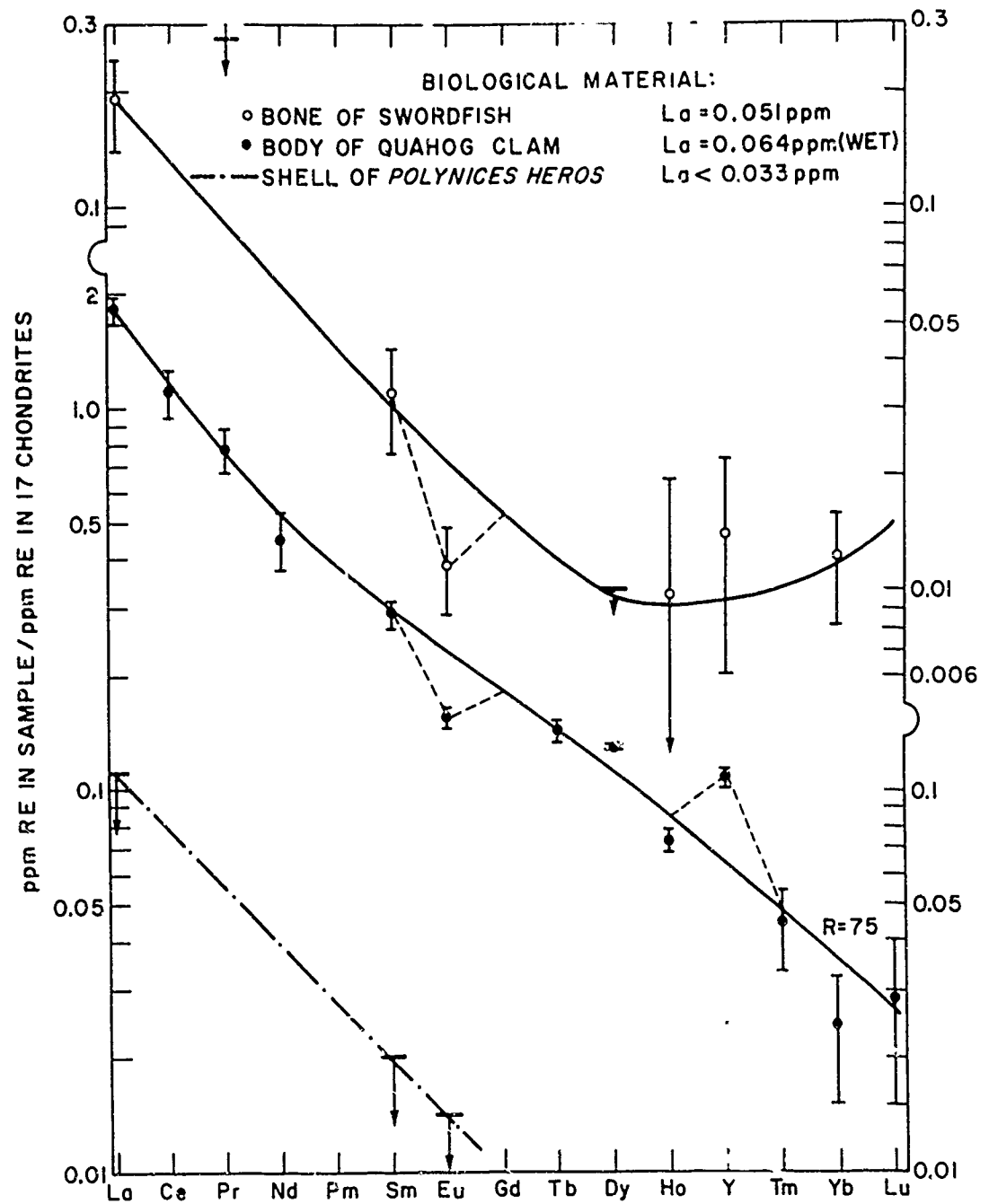


FIG. 9

Ratios of the RE abundances in manganese nodules: two from the Indian Ocean, one Pacific and one Atlantic, to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. The data for the Indian Ocean nodules (of which only the outer manganese-rich layers were analyzed for RE) are from Pachadzhnov et al. (1963), for the Pacific Horizon nodule from Goldberg et al. (1963) and for the Atlantic Caryn Peak nodule see Table 4.

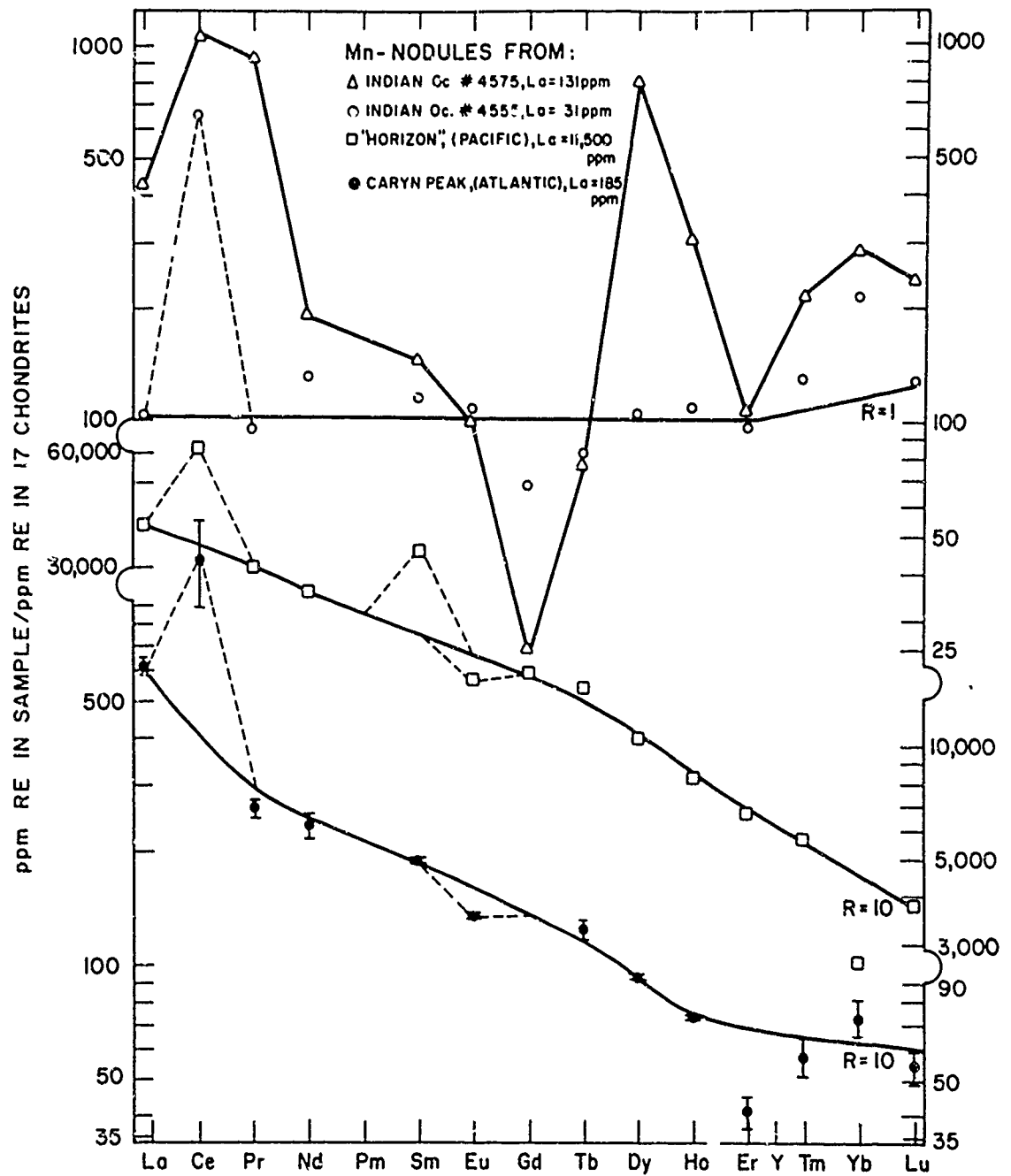


FIG. 10

Ratios of the RE abundances in Atlantic sea-water fractions: sea-water from 1100 m depth filtered through a  $0.45\mu$  -pore Millipore filter, solids  $>0.45\mu$  filtered out from same sea-water, the undialyzable fraction of similarly filtered sea-water from 700 m depth (same location), and in a Pacific unfiltered sea-water from 100 m depth, to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. Data on the Atlantic samples are given in Table 5; data on the Pacific sea-water are from Schmitt and Smith (1962); Goldberg et al. (1963). Arrows pointing down indicate gross values the blanks of which were below limit of detection but non-negligible. The large bar shows the gross value and the error bar above it shows its upper limit of error.

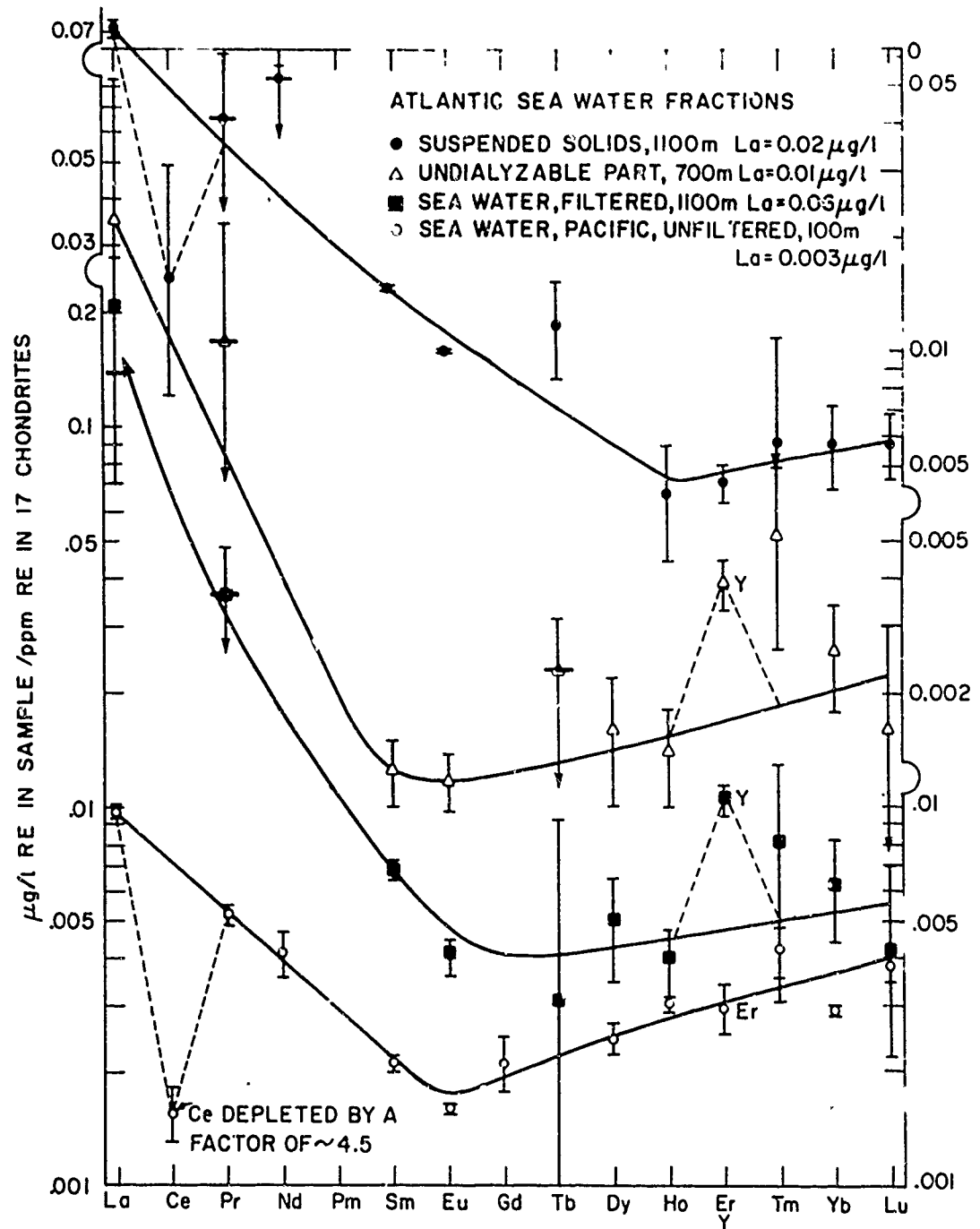
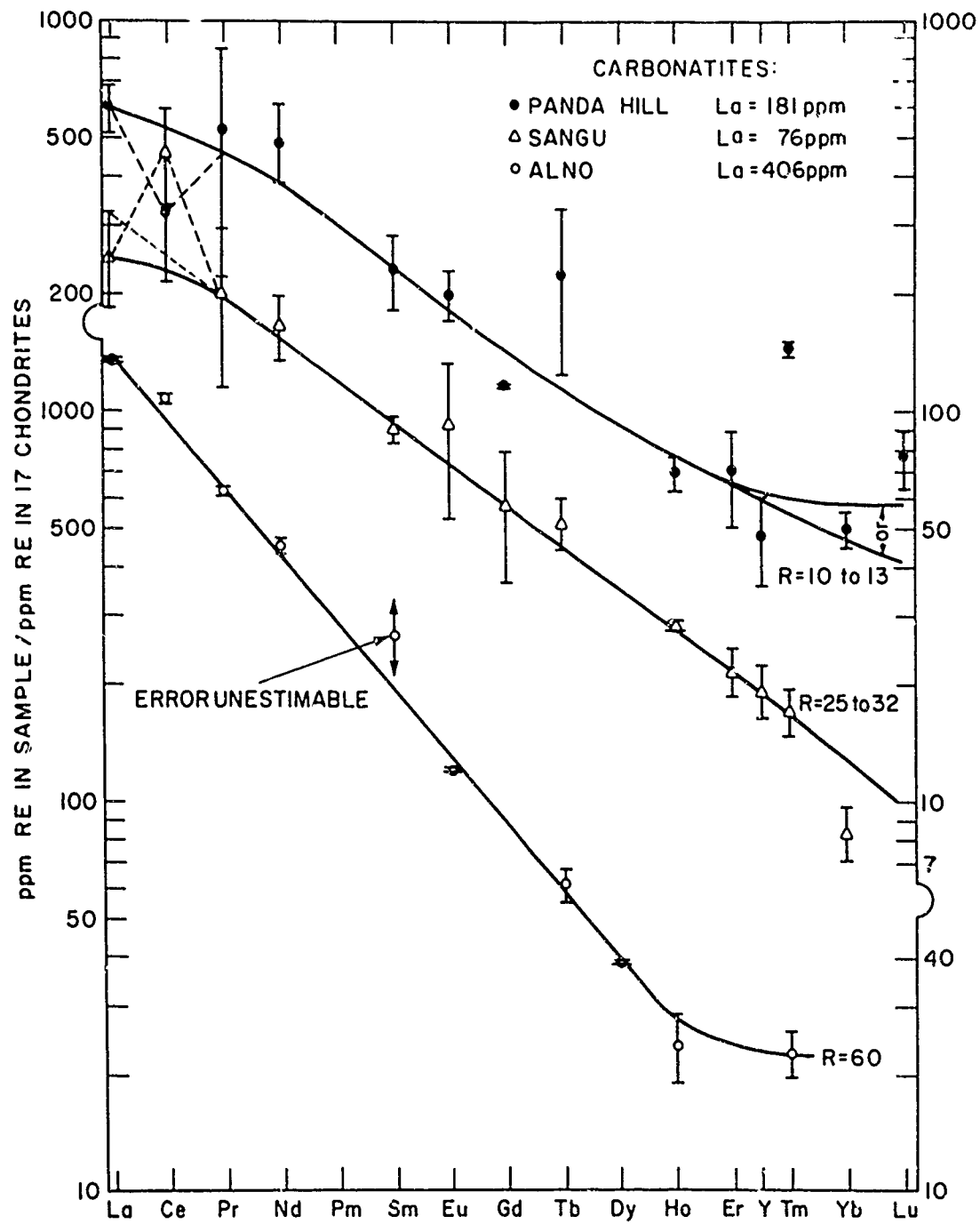


FIG. 11

Ratios of the RE abundances in carbonatites from Sangu and Panda Hill (Tanganyika) and from Alnø (Norway) to the corresponding RE abundances in 17 chondrites, plotted on a logarithmic scale as a function of atomic number. Data on the first two are from Schofield and Haskin (1964); for data on Alnø see Table 4.



### 3.2 General remarks on RE in the sedimentary cycle.

Until the beginning of this decade the only complete RE analyses of sedimentary materials were three analyses of composites of European and Japanese shales made by Minami in 1935. Their RE distributions were rather close and the inference made by Goldschmidt and accepted for almost thirty years was that the RE distribution in all sediments is practically uniform and that the average of those three shale composites represents it. This distribution was even quoted as representative of the whole earth's crust. Sahama (1945) reported a very similar distribution in a sediment composite from Finnish Lappland. (See Fig. 6 in Coryell et al., 1963.)

In 1953 Ostroumov reported analyses of La through Dy for 7 Black Sea sediment samples which were rather uniform in their distribution patterns but differed noticeably from the shale average. In 1960 Graf reported one complete RE analysis of a New Mexico limestone and its pattern was close to that in the Black Sea sediments. (See Fig. 6, op.cit.) Yershov (1961) reported the RE distribution in a coal in which there was a pronounced enrichment of the heavy RE and especially Y compared to Minami's shales, and Kochenov and Zinov'ev (1960) reported the RE in fish bone detritus whose pattern differed greatly from the RE pattern in fish bone detritus reported by Bloch (1961).

To give a more satisfactory coverage of RE of different sediment types, locations and ages Haskin and Gehl (1962) analyzed 10 different sedimentary rocks including a limestone, a marble, a carbonate sediment from Florida Bay, a quartzite, 3 sandstones, and 2 shales. The authors regarded seven of the samples as having rather uniform distributions and averaged their RE contents to yield an "average sedimentary RE distribution." The three rejected samples were Precambrian and the authors tentatively attributed the deviations of their RE patterns from the average to the early time of their formation, saying that: "Possibly in such old material selective leaching has occurred, or perhaps the sediments were formed before the RE in the crust were as well mixed as they now are." Taylor (1964) and Fleischer (1965) have proposed new crustal RE averages based on the average distribution given by Haskin and Gehl (op. cit.) but differing in absolute values.

Additional 6 RE analyses of sedimentary materials have been reported by Schofield and Haskin (1964), and RE analyses of marine sedimentary materials have been reported by Goldberg and Arrhenius (1958) (only La, Y, Yb); El Wakeel and Riley (1961) (only La, Ce); Goldberg et al. (1963); Semenov et al. (1962); Pachadzhnov et al. (1963) and Wildeman and Haskin (1965). In the course of discussion of our results the work of all these authors is used extensively for comparisons.

Close inspection of chondrite-normalized plots of the reported RE distributions in all the single samples as well as in the averages given by some authors and in composite samples brought us to the following basic conclusion: averages of many different sedimentary samples and sample composites tend to have similar RE patterns, but the RE patterns and absolute abundances of individual sedimentary materials vary considerably. (The same generalization, incidentally, holds true for acidic igneous rocks - see Chase et al, op. cit., Fleischer, op. cit.) Clays seem to vary over a narrower range than other materials and their absolute RE content is much higher than in other sedimentary materials except shales, phosphorites and manganese nodules. The clay RE pattern therefore overshadows any other pattern whenever a rock or sediment (e.g. calcareous and diatomaceous oozes) contains even as little as 10% clay, giving an exaggerated impression of the extent of RE uniformity among individual sedimentary materials.

For problems in which the crust is regarded as one whole it is important to reveal and stress the RE pattern characteristics which crustal materials have in common, but when we strive to understand the behavior of the RE and the various phases of their geochemical cycle in the crust itself it is the differences of the RE patterns of different materials that must be found, emphasized and understood.

Some of the similarities among terrestrial materials analyzed so far are as follows. With rare exceptions, they are all fractionated with respect to chondrites so that chondrite-normalized curves have negative slopes, and the fractionation of the light RE ("Ce group") is much more pronounced than that of the heavy RE ("Y group"). The latter group is often horizontal on chondrite-normalized curves, but in general varies from a slightly negative slope (e.g. figs. 4, 5) to a slightly positive one (fig. 10 except bottom curve). In extreme cases the Y group too becomes strongly fractionated: in a clam (fig. 8) a manganese nodule (Horizon, fig. 9), some carbonatites (fig. 11), most nepheline syenites and some granites, notably G-1 (Haskin and Gehl; Towell et al., 1965), with a steep negative slope, whereas in Pacific sea-water (fig. 10, bottom curve) and some eclogites (Schmitt et al., 1963) with a pronounced positive slope. The cases of strong fractionation of the Y group and particularly fractionation with a positive slope are, however, exceptions in the data available so far.

The features that most sediments have in common which, as mentioned above, are illustrated well by the patterns in figs. 4, 5, can be understood as the product of mixing of weathering products of the igneous rocks, part of which are strongly fractionated with an almost straight-line negative slope and very rich in the light RE end (most nepheline syenites and some, not all,

granites), and part quite mildly fractionated, with a much smaller light RE content but an appreciably larger heavy RE content (most basic and intermediate rocks). The superposition of such two patterns would result in the concave-up curves of figs. 4,5. (There seems to be no need to explain the concave shape of these curves by selective removal of Sm and its neighbors by some hypothetical material no sample of which has been found yet, as some authors have done.)

Thus, there is enough uniformity in crustal and particularly in sedimentary materials to contrast the average crustal RE abundances with the RE abundances and patterns in different classes of meteorites (Schmitt et al., 1963) and, quite probably, in the earth's mantle and core. Besides the different distribution the chondrites contain about 2 orders of magnitude less RE than the average crust. Two achondrites have a positive, concave-up slope and the Norton County Ca-poor achondrite has a positive, convex-up slope in its chondrite-normalized RE pattern, expected to occur in solid residues after partial melting and removal of the melt (Masuda, 1963, and J.G. Schilling, personal communication, 1964). The mantle probably has a similar RE distribution and absolute values similar to those in chondrites, whereas the core quite probably resembles the iron meteorites, whose RE content is 1-2 orders of magnitude lower than in chondrites.

The differences among sedimentary materials, from which we can hope to learn about the geochemical behavior of RE and later, possibly, about the geochemical history of the materials themselves, can be classified into four groups (all based on chondrite-normalized plots); namely differences in:

1. Degree of fractionation from light end to heavy end;
2. Exact shape of the RE distribution curve (degree and direction of curvature);
3. Enrichment, depletion or normality of Ce, Eu and Y relative to their adjacent elements (Y placed arbitrarily with Er);
4. Absolute RE content.

It is useful to have a numerical measure to compare various degrees of fractionation. We have defined the following "fractionation index":

Fractionation index = ratio of the highest part (usually La) to the lowest part (often an almost horizontal line through several heavy RE) of the chondrite-normalized RE distribution curve.

This index is preferable to the ratio  $\frac{\sum \text{Ce earths}}{\sum \text{Y earths}}$ , used extensively as an index of fractionation in most Russian work on RE abundances, because it is not affected by single element anomalies.

Anomalies in Ce and Y contents, which occur rather often, bias very strongly the  $\frac{\sum Ce}{\sum Y}$  ratio since the normal Ce content is about 40% of  $\sum Ce$ , and the normal Y content is about 75% of  $\sum Y$ .

The fractionation index as defined above is usually determinable to  $\pm 10\%$  and is only rarely uncertain to as much as  $\pm 20\%$ ; the uncertainty stems from the analytical errors given for the RE values and/or the scatter of the points, mainly at the heavy end, which result in some arbitrariness in the location of the "best" smooth curve. Its value is indicated at the right end of each curve in all figures with the designation R (e.g. R=5).

In sedimentary rocks the fractionation index (abbreviated below to "fr. in.") varies from about 2 to about 20, the majority falling between 5 and 15. In Table 6 the variability is illustrated by the fr. indices of 6 out of the 7 sediments from which Haskin and Gehl (1962) derived their sediment average, of three shale composites and of several manganese nodules. In most marine sediment samples with a considerable clay content for which complete RE analyses are available the fr. in. has so far been found to vary much less, only from about 5 to 6.5 (see 3.3.2 and figs. 1,2). It seems likely that non-clay components of the sediments have different RE patterns, but these have been swamped by the clay pattern. To learn about the behavior of RE during their sojourn

TABLE 6

La contents and fractionation indices of  
some sedimentary materials

Material	ppm La	fr.in.	Remarks	Ref.
Calcareous sediment	3.5	10		(1)
Leavenworth limestone	3.6	6.7		(1)
Antarctic marble	7	5		(1)
(Mississippian) sandstone	15	3.5		(1)
(Tertiary) sandstone	10.5	6 to 8	uncertain since points zig-zag	(1)
Kansas shale	20	8		(1)
"Average of sediments"	—	6		(1)
Composite of N.Amer. shales	39	7		(2)
Shale composite I	18	4		(3)
Shale composite 1I	12	5		(3)
Manganese nodules from:				
Atlantic, Caryn Peak	185	11	curve concave up	(4)
Pacific, <u>Horizon</u>	11,500	10	curve convex up	(5)
Indian Ocean, no.4555	31	1		(6)
Indian Ocean, no.4575	130	1.5	many points seem questionable	(6)
Pacific, I	235	4	only La, Sm, Eu determined	(7)
Pacific, II	314	6	" " "	(7)

References: (1) Haskin and Gehl (1962); (2) Wildeman and Haskin (1965); (3) Minami (1935); (4) This work; (5) Goldberg et al. (1936); (6) Pachadzhnov et al. (1963); (7) Kawashima et al. (1961)

in the marine environment one must separate out the various components of sediments, e.g. tests and skeletons of different organisms, underwater-volcanogenic materials, etc. and, if possible, differentiate between the terrigenous (detrital) and hydrogenous phases of the clays themselves and determine the RE abundances in each such component. Hurley et al. arrived at a similar conclusion based on their K-Ar work reported in a series of papers (1963).

The work reported here was undertaken with the point of view presented in this section, aiming mainly to contribute to the knowledge and understanding of the details of behavior of RE in the marine environment rather than at obtaining averages of global scope.

Balashov et al. (1964) in a paper which recently became available to the author likewise gave an evaluation of published RE data on sedimentary materials stressing their variability. Their group has begun an extensive study of the behavior of RE in the sedimentary cycle the beginning of which is reported in this paper. It gives about 40 RE analyses of exposed sedimentary rock samples and sample composites from an area the geology of which is known in great detail and on which much previous geochemical information exists, and it correlates the different RE patterns found with paleoclimatic differences. A summary of their results and conclusions is given in Appendix A.

### 3.3 Distributions of RE in the marine environment.

For knowing the global geochemical balance of RE information on RE in marine clays plus information on RE in shales is most important, since shales and marine clays are the largest repositories of RE in the sedimentary cycle; their RE concentration is about an order of magnitude higher than in sandstones, limestones, and deep-sea calcareous phases, and their bulk is larger: there is more shale than sandstone and limestone, and more pelagic clay than all pelagic completely authigenic materials like calcareous tests, siliceous tests, phosphorites, etc. (Estimates of the total bulk of manganese nodules vary very widely; they may be important as a RE-holding phase where they occur in very large quantities since they have a 2 to 5-fold higher RE content than the marine clays analyzed in this work and 3 to 8-fold higher than those reported by Wildeman and Haskin (op. cit.). This statement is based on RE contents of 4 out of 5 nodules on which we have RE data, excluding one nodule with 9% RE). According to a combination of estimates by Poldervaart (1955) and Goldberg (1961) the bulk of shales is about 4 times larger than the bulk of pelagic clay; the RE content of pelagic clays is roughly 3 times higher than that of shales (according to the still rather limited data available), and thus very roughly the bulk of RE in sediments is divided about

evenly between the shales and the pelagic clays; they contain between them the bulk of the RE weathered off the crust in geologic time.

Shales and pelagic clays can be expected to differ in RE content and distribution as a result of their genetic differences. For the purpose of this discussion it is sufficient to mention only a few features of the genesis of shales and pelagic clays, which amount to a very sketchy and oversimplified picture of these complex processes. Shales are mostly marine shelf sediments (and some are purely terrestrial), whereas the clays are pelagic, as their name describes. A shale bed consists basically of particles of weathered igneous and sedimentary rocks washed off by runoff water and transported by it to the sea, where they sank on the continental shelf generally not very far from their source area and underwent the sequence of events that turned them eventually into a shale. Thus the source area of a shale bed is a part, varying in size, of one continent, and the composition of the shale is largely determined by the composition of the source rocks in this, relatively limited, area, plus the organogenic and hydrogenic components originating in the shelf area, minus components lost by leaching during transport and during the subsequent stages of formation and denudation of the shale.

The origins of the terrigenous component of pelagic clays, the main agents of transport to the sites where the clays are deposited and the extent to which this component becomes reworked under way and after deposition are all still rather controversial. It seems, however, that according to all views the individual aluminosilicate particles of a pelagic clay sample are derived from sources greatly spread in area, often from more than one continent, and thus originally very variegated petrologically and compositionally. On their way to the sea bottom, the particles of a pelagic clay will have traversed a water column usually consisting of a stack of currents flowing in different directions and carrying waters often differing in their contents of oxygen, trace elements and dissolved organics, all of which can interact with and/or become adsorbed on the suspended clay particles in the course of their very slow settling.

These genetic differences between a shale and a pelagic clay lead us to expect much more uniform compositions in the latter, plus a higher RE content.

Besides the aluminosilicate component a pelagic clay

will usually contain Fe and/or Mn hydroxides with all their coprecipitated trace elements, organogenic debris, underwater volcanism products and some extra-terrestrial dust and micro-meteorites. It is mainly the non-aluminosilicate phases that can be expected to produce variability in the RE compositions of pelagic sediments.

After burial of the particles of a pelagic sediment, diagenesis sets in. The pH decreases slightly (7 to 8), but the Eh drops considerably, from +0.4v in bottom seawater to various values down to -0.2v. (Pachadzhanyan, 1963, quoting papers presented at the International Geologic Congress in 1960.) This causes solubilization of some components and fixation of others. It cannot affect Eu because of the extremely low concentration of Eu in seawater, and not other RE directly since their valencies are not variable, but it may partly solubilize Ce, and iron and manganese hydroxides that included coprecipitated RE, and release them into the pore solution. The RE would then get partly adsorbed on the clay surfaces further enlarging the RE concentration of the clay phase, and partly perhaps escape

upward (by ionic migration caused by a concentration gradient) into the bottom waters. This might be the cause of the increase of RE concentration with depth in sea-water found by Balashov and Khitrov (1960) and again by Schmitt and Smith (1962).

The shales and clays analyzed for all (or most) RE so far, have RE characteristics in agreement with the foregoing considerations: the RE distributions and especially the fractionation indices are much more alike in the clays than in the shales, and the RE content of clays (when recalculated or estimated relative to the weight of actual clay, eliminating the weight of RE-poor components like carbonates, diatoms, radiolaria, etc.) is more uniform and higher than that in shales.

Exceptions to the generalizations can be expected, as mentioned. Special local conditions of winds, currents and biomass productivity should result in deviation of the RE pattern of some pelagic clays from the most common one. Evidence that interesting differences in RE distribution in distinct marine phases can be expected is given, among others, by Arrhenius (1964) who reported very high enrichments and unique RE distributions in microcrystalline apatite in pelagic fish-bones; neither an enrichment nor a unique distribution was found in fish-bones buried

under shallow water, where lower partial CO<sub>2</sub> pressures do not suffice to cause the apatite crystallites to dissolve. These results point out again the importance and interest of conducting RE investigations on distinct phases rather than on whole-core samples.

Differences in RE distribution can also be expected in areas of extensive under-water vulcanism, where lavas and hydrothermal solutions of various compositions are poured into the sea and partly dissolve in it. None of the 12 marine samples considered in 3.3.2 came from such an area. In fact, half of them came from a rather small area in the North-East Atlantic.

Obviously, a much more comprehensive geographic distribution of pelagic sediments and their various constituent phases must be analyzed for RE to gain a fuller understanding of the geochemical paths of the RE group in the marine environment.

#### 3.3.1 Three pelagic red clays and a diatomaceous ooze.

(samples V5, V2, V9, V6)

Cores and samples description. The two cores sampled consist largely ( > 90%) of "red" clay, quite homogeneous in particle size and color, accumulated at great depths. Absence of visual evidence of disturbance by slumping or by turbidity currents points to continuous, particle-by-particle deposition (Ericson et al, 1961). The color is slightly reddish brown.

TABLE 7

Information on samples discussed in 3.3.1

Core Location	Core No.	Water Depth	Sample	Sample Depth in core	Age Difference	CaCO <sub>3</sub> and NaCl determinations (by Ku)	
						Depth in core	
S. Indian Ocean	V16-75	4630 m	V5	53-54 cm	{ V5 to V2 ~ 2 million years	50-60 cm	4%
	"	"	V2	1223-4 cm		1212-1217 cm	8%
							5.5%
Antarctic	V16-32	4590 m	V9	985-6 cm	{ Top to V9 1-2 m.y.		not detd.
(=S.E. Pacific)	"	"	V6	65-66 cm			not detd.

Concurrent work was done on these cores by T. Ku (1965) at Lamont Geological Observatory, on the problem of  $U^{234}$  migration along the sedimentary column. He determined U, Th,  $U^{234}(Io)$  and calculated possible ages and rates of deposition assuming various plausible  $U^{234}$  migration rates and a series of possible boundary conditions, and compared them to the rates of deposition of neighboring cores determined by Goldberg et al. (1962). Some of Ku's results, pertinent to our work, are tabulated in Table 7.

Discussion of RE results in the red clays V5, V2, V9.

(See Table 2 and fig. 1)

Comparison of the chondrite-normalized plots of the three samples shows striking similarities. One point of comparison, the exact RE distribution, is uncertain in the case of V9 due to the large errors of Pr and Nd and lack of data on Dy, Y, Tm in it.

The similarities are in the following points:

1. Very similar fractionation indices: 5.8, 5.7, 5.9, all  $\pm 0.2$ , for V5, V2 and V9, respectively;
2. Very similar curvature of the chondrite-normalized RE distribution curve;
3. Very similar La/Sm ratios, lower than in most materials with a similar fractionation index; 4.05, 4.10, 4.0 in V5, V2, V9, respectively;
4. Very similar Sm/Eu ratios in V2 and V5, higher in V9: 3.75, 3.83, 4.55 in V5, V2, V9. Eu is slightly depleted, 15% - 20% below its normal position on the distribution curve;

5. A small, similar Ce depletion is indicated in V5 and V2, but the large errors make it uncertain. Ce in V9 is almost normal, but with a similar uncertainty.

Since V2 and V5 were about 12 m apart in depth and about 2 million years apart in time of deposition, and both were separated from V9 by more than a quarter of the earth's circumference, it is probably most reasonable to consider the extremeness of the similarity among them as coincidental. Only if more samples of the same cores prove to fall into the same extremely narrow range of RE variability will conclusions and explanations accounting for the extreme narrowness of the range become warranted. Extensive post-depositional RE migration along the sedimentary column would be one of the processes implied; another would be an extremely wide variety of terrestrial source areas for the material in each of the cores.

RE in the diatomaceous ooze.

Sample description. The sample, V6, came from 65-66 cm depth in the same core as sample V9 - core no. V16-132, from the South Pacific part of the Antarctic Ocean, 4590 m water depth.

Below ~1 m the core consists largely of visually homogeneous "red clay." Higher it turns discontinuously into a diatomaceous ooze, containing 60 to 80% organic silica (rough estimate from inspection under the microscope). The change is

believed to have been due to a change in temperature and/or nutrient supply in the euphotic layer above which greatly increased its biological productivity. The rate of clay deposition may not have changed, but the much faster deposition of the diatom remains caused the clay percentage in the core to drop. (J. Hayes, personal communication). No analyses of the clay in the core are available to give a clue as to whether the clays depositing below and above the organic discontinuity were the same or different.

Discussion of RE in sample V6. The sample was selected in order to see how the RE distribution and content in a diatomaceous ooze compared to those in red clays and globigerina oozes. Also, since a "pure red clay" sample (V9) was taken from the same core, a site variability effect had a better chance of being eliminated. No RE analysis of pure diatoms is known, but the lack of chemical resemblance between Si and RE, the larger radius of the latter, and the low Ca content of diatoms all seem to diminish the chances of any considerable RE content in them. Thus, a RE distribution similar to that in V9 with the absolute RE content diminished proportionally to the clay content were expected as most likely.

Comparison of the chondrite-normalized plots of V6 and V9 shows at a glance that this expectation was not borne out. The distribution of the RE Sm through Yb is, indeed, identical

in the two samples within limit of error, with the absolute values in V6 being about 25% of those in V9. La and Ce, however, are relatively considerably higher in V6 (~40% of La and Ce in V9), resulting in an overall fractionation index of  $11.5 \pm .5$  in V6, versus  $5.9 \pm .2$  in V9. This takes the V6 distribution completely out of the range of fractionation indices of the 12 oceanic samples discussed below (3.3.2), eleven of which ranged from 5 to 6.7 (the twelfth had an index of 8). With no values for Pr and Nd, this index difference is based only on the values for La and Ce, but in the nature of our analytical procedure La is one of the values that seem most reliable and the normalized Ce point lying on a smooth line between La and Sm seems to be a good confirmation of the validity of both the La and the Ce points. Some EDTA-treated samples described below (E2, A1-A4) have RE distributions and fractionation indices close to that in V6. This seems to lend it additional credibility, albeit indirectly.

We can see three possible explanations of the RE distribution difference between V9 and most other marine sediments analyzed so far on one hand, and V6 on the other:

- 1) The changed conditions in the euphotic layer which resulted in the high diatom productivity consisted of changes in currents; the different current pattern brought and deposited at the core site clay particles from a different set of source areas

and these contained a different combined RE pattern than the clays in V9. This explanation assumes that the whole-sample RE pattern in V6 is practically that of its clay component, because the RE content of diatoms is so low that they hardly affect the whole-sample RE distribution. This would also explain the lack of resemblance between the RE pattern of the diatomaceous ooze analyzed by Wildeman and Haskin (op. cit.) which had a fr. in.  $5.3 \pm 0.3$ , Eu normal, and that of V6 in which the fr. in. was  $11.5 \pm 0.5$  and Eu was depleted: the RE contributions of the diatoms in both samples are completely masked, and the clay components' RE patterns are different.

2) The extreme fractionation (fr. index 75) found in a clam (see fig. 8) implies at least a possibility that diatoms, or some species of diatoms, have very high RE fr. ind. like the clam. If their La content is above 5 ppm then a mixture of 75% of diatoms plus 25% of the V9 clay would have the RE distribution of V6.

The diatoms in the other diatomaceous ooze sample reported (op. cit.) would then be assumed to have either a RE distribution radically different from that of the diatoms in V6, or a 3 to 5-fold lower absolute RE content, or they would have to comprise a much smaller percentage of the total sample. However, a large enough difference between the RE compositions and contents

of the clay components alone of the two samples could suffice to produce the different whole-sample distribution even in this case.

3) V6 may have an unknown component (which the other diatomaceous ooze doesn't have), which is relatively rich in RE and has a strongly fractionated RE pattern.

Intuitively explanation (1) is most plausible, but only a RE analysis of a clay or diatom concentrate from V6 or RE analyses of other diatoms adequately free from clay will enable us to understand better the RE distribution in sample V6.

In general, sample V6 may be a good illustration of the statement made in 3.3, that a variety of local causes can be expected to produce pelagic sediments with RE distributions different from the most prevalent ones. Its difference from the 12 samples discussed in 3.3.2 may indicate that the core from which it came is of special interest in its geochemistry and sedimentation history, and thus especially worth while studying in more detail. At least one more sample of marine origin is known at present whose RE fractionation pattern is outside the range of the 12 samples below. It is a phosphorite from the Permian Phosphoria formation in Wyoming analyzed by Schofield and Haskin (1964). Its fr. ind. is 8.9, whereas that of the Baja California phosphorite (fig. 2) is 5.0.

It is also possible that when a larger number of marine

core samples representing a comprehensive geographic grid (instead of isolated corners of the oceans) and a wider cross section of underwater geologic and biological conditions are analyzed for RE, the RE patterns in these samples will prove to be much less exceptional than they seem to be at present.

3.3.2 Discussion of twelve marine sediment samples with  
very similar RE patterns (see figs. 1,2)

Comparison of the three red clay samples analyzed for RE in this work (fig. 1) with the 8 marine samples reported by Wildeman and Haskin (op. cit.) and with a phosphorite from Baja California analyzed by Schmitt (Goldberg et al., 1963) (fig. 2) shows immediately that these samples are more uniform in RE pattern than any comparably large and geographically scattered set of single samples of shales + limestones + sandstones. Their overall variability range is larger than in the three red clay samples reported here (and therefore the interpretation requirements are less stringent), yet it is narrow enough to be noticeable as a distinctive feature.

As discussed in 3.3, the genetic history of pelagic sediments makes considerable uniformity among them expectable.

Upon examining how these 12 samples compare in the five characteristics of similarity marking samples V5, V2 and V9,

we find the following:

1) The fractionation indices are the most prominent point of uniformity in this group of samples. In 11 out of the 12 samples they are in the range 5 - 6.7; the one outside this range is 8. This seems to contrast with shales, where in three sample composites and one single shale sample for which RE data are available this index ranges from 4 to 8 (see Table 2).

2) The (concave-up) curvature of the RE pattern plots is mostly larger (see fig. 2) than in the three samples V5, V2, V9 (fig. 1) analyzed in this work, i.e. in these three samples the contents of Sm and its neighboring elements are relatively higher than in the other nine.

In three samples out of the latter, whose RE patterns are drawn in the top three plots of fig. 2 and which include the one sample with fr. ind. 8, the curves have inflections, whereas in all the other plots in fig. 2 the curves are homogeneous. This may possibly be related to the locations of the cores: the three samples with inflected curves came from the Brazil and Argentina basins in the Atlantic, whereas the other six came from one corner of the Pacific ocean; V5, V2 and V9 came, as mentioned before, from the Antarctic and the southernmost part of the Indian ocean. Tentatively we may speculate that sediments in the pelagic areas open to the main Pacific-Antarctic global ocean stretches became

more uniform in their RE patterns than those in the relatively more enclosed Atlantic.

An inflection of the RE curve at Sm appears also in samples of Atlantic calcareous tests analyzed in this work (fig. 5). One is tempted to see in this inflection a general characteristic of Atlantic sediments with a high proportion of hydrogenous RE, but such a generalization could justifiably be made only on the basis of a much larger number of samples.

3) The La/Sm ratio in the 9 non-Atlantic samples found above as most uniform on the basis of their RE distribution curve shapes ranges from 4.0 to 5.0 ( $\pm$  10% to 20%). Of the 3 Atlantic samples, considered different, this ratio is 4.44 in one and 5.4, 5.8 in the two others, respectively. In sandstone, marble and shale with similar fractionation indices the La/Sm ratio is close to 6 and over; hence, again, the hydrogenous component seems to tend to get enriched in Sm and its neighboring elements, as pointed out by Goldberg et al. (1963). In samples V5, V2 and V9 this enrichment was most pronounced - their La/Sm ratios were lowest.

4) The range of Sm/Eu variation in the 12 marine samples is comparable to that in shales, sandstones and limestones. It is relatively narrow compared to its range in igneous minerals and in some special sedimentary environments (e.g. some coals, some sulfide environments) where large Eu depletions and enrichments are encountered.

In the 12 marine sediments considered here Eu varies from normal to about 20% depletion; in one Atlantic brown clay it is possibly depleted by 35% but the errors of Sm and Eu are about  $\pm 20\%$  each, making the extent of actual depletion in this sample quite uncertain.

In summary, the Eu in most sediments is not normal (as has been believed), but its depletion is usually not very large. It is noteworthy that in Pacific sea-water (fig. 10) it is also somewhat (15% - 20%) depleted. In the Atlantic sea-water analyzed in this work (fig. 10) the errors of the RE heavier than Eu are too large to tell whether Eu is normal or not.

5) Ce values are available for 8 out of the 12 marine samples under consideration. Of these 3 are normal with respect to the general RE distribution curve, 3 are depleted by about 20% but are within limit of error from normal, and 2 are depleted by 28% and 35%, respectively, well outside their limit of error. The latter are one of two samples from a core of Atlantic brown clay, the other of which has normal Ce, and one sample of Pacific Radiolaria-rich clay. No regular pattern is seen in these results.

The large depletion of Ce in the Pacific sea-water, in the suspension filtered out of sea-water (fig. 10) and in the globigerina sample tests (fig. 5) seems to show that Ce depletion is characteristic of sea-water and hydrogenous phases. Mn nodules,

on the other hand, are selectively enriched in Ce and by inference we may expect that small particles of Fe-Mn hydroxides which are ubiquitous in the sea will also be enriched in Ce. Thus any sediment accumulating on the sea bottom will contain material with normal Ce (terrigenous), a component depleted in Ce (hydrogenous non-manganic) and a component enriched in Ce (ferro-manganic), and the relative proportions of these three will determine its overall Ce content relative to the other RE. Many different proportion-combinations will yield the same relative whole-sample Ce and only extreme depletion or enrichment will point to a definite predominance of the hydrogenous or the ferro-manganic component respectively.

Note: Selective Ce enrichment in the hydrogenous hydroxide phases is presumed to be contingent on the presence of manganese, since non-manganous ferric hydroxide practically does not fractionate Ce from the other RE.

6) Yttrium is largely normal among the other heavy RE in the 11 clay-containing samples, but it is enriched almost 2-fold in the phosphorite (fig. 2, bottom curve). This will be discussed below (3.6) where additional samples with a Y enrichment are described.

It should be repeatedly noted that the five samples in

fig. 2 that have most uniform features and compare best with V5, V2 and V9 of fig. 1, all necessarily contained a considerable proportion of clay although they are labelled according to their non-clay components (radiolaria, diatomaceous ooze, globigerina ooze) or by origin (terrigenous). As pointed out before, clay is by more than one order of magnitude richer in RE than the several other components and the reported RE distributions are largely those of the clay component (plus the ferromanganous phase, if any), only slightly modified by the small  $R^n$  contribution from other, even though bulkier, components. The RE distributions in the latter will become known only when they are analyzed for RE after adequate separation from clay and other RE-rich phases. Some of the data obtained in this work and discussed below indicate that the RE patterns of organogenic phases, especially, may be expected to be distinctly different from that of the clays. This is to be expected on theoretical grounds too, since the mechanism of RE uptake and the RE species (ionic, colloidal, metal-organic complex) preferentially taken up by clays and by different organisms cannot all be the same.

With this reservation clearly in mind, the generalization seems to be warranted that the whole-sample pelagic sediments are mostly rather uniform in their RE patterns, as expected from the homogenizing properties of the processes acting on them in the

sea-water and the agents that bring them to their eventual settling site. Before this can be established as a rule, however, RE analyses are needed of a much more comprehensive selection of samples adequately representing all pelagic sediments geographically and compositionally.

It should be mentioned in this context that the contents of La, Y and Yb determined spectrographically in over 30 Pacific cores reported by Goldberg and Arrhenius (1958) seem to exhibit a definite variation with location. Samples coming from north of roughly the  $25^{\circ}\text{N}$  parallel, average 5 times less yttrium (0.004%) than samples from the south of that parallel (0.020%) and La and Yb could be determined only in the latter. All the Pacific samples presented in fig. 2 also came from northern latitudes higher than  $25^{\circ}\text{N}$ , and their Y values are in the same low range as those of the northern samples reported by Goldberg and Arrhenius. The Y/La and Yb/La ratios in the RE-rich, southern samples tended to be about twice higher than in the 12 samples discussed in this section. Wakeel and Riley (1961) reported La values in Atlantic clays about twice higher than in these 12 samples; the accuracy of their La and Ce spectrographic analyses may not have been quite satisfactory, since their La/Ce ratios range from 8 to  $1/8$ , a range very much wider than all other known RE analyses have shown. Both these sets of single RE results re-emphasize, however, the need of caution

in making general conclusions on the basis of the still very scanty RE data available on sedimentary materials in general and marine and pelagic in particular. As mentioned before, a few marine samples are already known to have RE patterns outside the narrow range of the 12 samples discussed here, and additional work may show that such "exceptions" are common.

3.3.3 Results of EDTA-treatment of "red clays" V2 and V9.  
(Attempt at differentiation between hydrogenous  
and terrigenous RE) .

The EDTA-treatment of samples V2 and V9 yielding E2 and E9 as described in 2.1.2 was applied aiming to try to differentiate between the RE bound in the internal structure of the clay - presumably detrital terrigenous - and the RE adsorbed on its surface - presumably hydrogenous - plus, possibly, the RE included in the ferromanganous phase, if any. "Red clay" samples V2 and V9 were selected for treatment because they were comparably old (in burial time) and therefore comparably reworked by post-depositional processes, and because their whole-sample RE abundances were similar (fig. 1).

Goldberg and Arrhenius (op. cit.) have attempted to determine, among other elements, the RE adsorbed in the exchange positions on pelagic clay by 6-hour treatment with a large volume of N ammonium acetate at 80°C. They found no La and Yb among the

ions thus replaced by ammonium ions (the "sorbate"), and only 0.4% of the original Y content of the samples, and inferred that "these elements do not occupy exchange positions". The easy sorption and desorption of Y tracer on clay, described in sec. 2.1.2, indicated, however, that the Y did occupy exchange positions there, and the fact that it was practically unexchangeable by ammonium shows only that they are held in those positions more strongly than other elements. A somewhat similar situation is reported by the authors for Mg which, they found, was held by the clay much more strongly than Ca. Likewise, they found that only a few tenths of a percent of the total Ti was exchangeable by ammonium, most likely for the same reason. Failure to detect any La and Yb in the "sorbate" was most probably due to the relatively high spectrographic limit of detection, not to any material difference between Y and the other RE in their behavior on the clay surface.

The same authors further submitted some of their samples to chelative dissolution by a 5% EDTA solution, stirred with the sample for 2 hours at 100°C. They found that this treatment dissolved most or all of the ferromanganese oxides, microcrystalline apatite and other minerals to varying degrees. They, therefore, interpreted the large losses of RE from some of the samples submitted to this treatment as indicating that the lost RE were all included in such minerals.

Wakeel and Riley (1961) found that this could not be the case, since according to published values on RE abundances in manganese nodules and apatite minerals the Mn and  $P_2O_5$  content of their samples could not account for more than 1/5 of the La and Ce they contained. They concluded that the remainder had to be associated with the clay minerals.

On the basis of the work of these authors and our own tracer experiments (2.1.2), we tentatively conclude that the low EDTA concentration and the room temperature at which the EDTA treatment of V2 and V9 was carried out resulted mainly in stripping the surface-adsorbed species from the clay minerals, partial dissolution of ferromanganese and apatite phases (if any were present) and, of course, leaching of soluble sea salts (about 5% in V2, unknown but probably similar in V9).

On examining the results (Table 2, figs. 3a and 3b) and disregarding at first the "humps" of relatively high Ce and Pr in E2 and E9, it is seen that E2 retained only  $\sim 1/3$  to  $1/6$  of the RE present in V2, and E9 retained, more uniformly, about  $1/4$  of the RE of V9. If indeed all the removed RE had been on the surface of the clay particles this result is rather striking, but not implausible. However, the possibility cannot be excluded that the EDTA leached out some internally bound RE (perhaps from disordered layers) in addition to stripping the surface-adsorbed part. Not

knowing the Mn contents of V2 and V9 we cannot decide how large a fraction of the EDTA-stripped RE, i.e.  $RE_{(V2-E2)}$  and  $RE_{(V9-E9)}$ , may have been enclosed in ferromanganese minerals. We can, however, speculate about the extent of possible leaching of internally bound RE: as noted before, shales, which presumably have a smaller hydrogenous component than pelagic clays, but whose terrigenous component should be roughly like that in clays, were so far found to contain 2 to 5 times less RE than pelagic clays and a part of these RE must also be surface bound. The EDTA-leached fractions retained 1/3 to 1/6 of the whole-sample RE, hence maximum 1/3 to 1/2 of the shale-equivalent RE may have been leached, assuming total absence of ferromanganese minerals. Presence of the latter must correspondingly reduce the maximum amount of RE that may have been leached from the original detrital RE content. Its part in the total RE stripped by the EDTA is less than 25% in any case.

The RE left in E2 and E9 are probably mostly terrigenous, - there is an uncertainty in the interpretation of this part too, however, since the heavier RE have higher chelation constants with EDTA, and thus may have been leached out preferentially, leaving relatively more of the lighter RE. The remaining RE pattern would then be more strongly fractionated, i.e. have a higher fractionation index than the terrigenous RE really had. The steep slope of the E2 RE distribution could thus have arisen as an artifact. However,

the slope of E9 is quite close to that of V9, possibly indicating that such an artifact does not, or at least need not, arise, and that the EDTA-treatment used does yield a sample in which the RE distribution of the terrigenous part of the sediment is fairly well represented except for cerium.

The behavior of Ce toward the EDTA treatment. The amount of Ce in E2 is almost the same as in V2, indicating probably that Ce, presumably in the +4 form is held by the clay surface much more strongly than the trivalent RE, and the EDTA could not strip it at all (in E2) or not as efficiently (in E9) as the other RE.

If the violet coloration of the EDTA solution by V9 mentioned in 2.1.2 was due to some components of ferromanganese minerals present there but not in V2, then part or all of the Ce that was stripped from V9 may have been in these minerals, whereas the Ce that was on the clay surface remained there, like in E2.

The Pr values in E2 and E9 are believed to be erroneously high.

In summary, this experiment shows that a very considerable fraction of the RE in pelagic clays is surface-adsorbed, but it also illustrates some possible pitfalls of chemical procedures for separating different components of a sediment. Acid leaching has been shown (Teh-Lung Ku, 1965) to be definitely unsatisfactory for

this purpose. Although the EDTA procedure has not been demonstrated here to be misleading for RE other than Ce (for Ce it seems to be so), careful experimenting with different RE tracers would be needed to determine exactly its effects. Physical separation procedures, depending on grain size (sieving and settling rates), on specific gravity, and hand picking where possible should probably be given preference wherever feasible.

3.3.4 Insoluble and globigerina tests samples from  
globigerina ooze core A180-74  
(Mid-Atlantic Ridge at equator, water depth 3330 m)

Core Description. The core is a typical "almost pure" globigerina ooze, with 80-90% acid-soluble material. It has all characteristics considered as evidence of undisturbed particle-by-particle deposition (no turbidity flows or slumping) and no evidence of carbonate dissolution according to Ericson et al. (1961). It has a considerable fraction, 20%-30% of coarse calcareous tests easily separable by wet-sieving, on which  $C^{14}$  ages have been determined for the top 2 m of the core. The relative water temperature in which the forams lived has been estimated by paleontological examination for the top 4.5 m of the core at 10 cm intervals, and interpreted to extend through the Last Glaciation well into the last warm Interglacial period. Insoluble material from the same core sections (different sectors) as used by us for RE

determinations was analyzed by Hurley et al. (1963) for K-Ar ages and proved to be incommensurably older than the foram tests deposited together with the insoluble; it was 160 to 330 million years old, and the authors regard it as wind-blown material, mainly the fine size fraction of terrestrial shales exposed in the Sahara.

The ages they determined are:

Sample corresponding to our:	Depth in core	Age, million years	Deposition ages (Foram ages)	Period
A1	95-100 cm	240	26,700 yrs.	Glacial
A2	197-200 cm	323	50,000 "	Glacial
A3	344-350 cm	233	100,000 "	Warm
A4	401-404 cm	163	120,000 "	Warm

Sample A2, the oldest, is believed to possibly represent a different source area and thus a changed wind pattern. The authors seem not sure that the age difference between A3 and A4 is real.

These age differences and, mainly, the source differences between the insoluble material (old, terrigenous) and the globigerina tests (young, hydrogenous) should be kept in mind. Clearly, no correlation of the RE in two such fractions from even the same core slice can be expected, since argon retention makes RE interchange unlikely.

Strontium has been determined for this core on whole-core and insoluble fraction samples by Turekian (1964). Assuming from previous studies that Sr in the  $>74\mu$  carbonate tests fraction is known and constant at 1200 ppm, he obtained by calculation values ranging from 2500 to 3700 ppm Sr for the  $<74\mu$  carbonate tests fraction. This result should be kept in mind, since a similar enrichment of RE in the  $25\mu - 75\mu$  tests fraction over the  $>75\mu$  tests fraction was found in this work.

For maximum utilization of information available on this core, we used available sectors of the same four core sections as were taken by Hurley et al., for the K-Ar age determinations on the insoluble fraction.

3.3.4a RE in EDTA-treated clays from core A180-74  
(Table 3, figure 4)

The possible implications of the experimental method used to obtain the clay fractions should be kept in mind for any evaluation of the RE-data on these fractions (see 2.1 and 3.3.4).

In the best case, these RE values are actually the true abundances of RE in the original detrital material before it had come in contact with natural waters. Their general distribution pattern resembles strongly that of the North American shale composite (Table 2), the similarity being strongest in A3, which has a fractionation index (8.1) closest to that of the shale (6.8).

A2 and A4 are more strongly fractionated and no light RE values are available for A1. Since shales vary in their RE fractionation index within at least a factor of 2, it would be very interesting to see whether a Sahara shale-composite RE pattern compares more closely with A2, A3 or A4 than the N. Am. shale-composite does. The Sahara shales are believed by Hurley et al. to be the most likely source of all or some of these clay samples. Such a RE-distribution similarity, if found, would indicate that the high "finger printing" potential many writers believe the RE must have, can indeed be realized. No complete RE analyses of any Sahara shales are available at present.

However, as stated before, the data on the results of EDTA treatment of the whole-core red clay samples V2 and V9 (yielding E2 and E9), as well as the presence of RE from the dissolved carbonate fraction in the solution in contact with the A1-A4 clays, bring to mind some mechanisms one or more of which may have modified the original (detrital) RE patterns of A1-A4. The mechanisms are as follows:

- 1) The higher chelation constants of EDTA with the heavier RE may result in uneven stripping of different RE from the surface and/or even leaching of the heavier RE from inside the clay particles. The depletion of the heavy RE in E2 compared to V2 and the rather strong RE fractionation in A2 to A4 might be

results of such preferential chelation. On the other hand, it is not unlikely that the RE pattern of the surface-adsorbed RE in V2 was actually very different from that inside the particles (much less fractionated, as some natural waters are - Robinson et al., 1958), and the difference between E2 and V2 is real, not an artifact of the EDTA treatment (cf. results of Balashov et al. 1964, summarized in Appendix A). The similarity of the RE patterns of V9 and E9 may indicate that selective leaching of the heavier RE by EDTA does not take place. The data at hand are insufficient for decision.

2) The very high Ce "enrichments" in E2 and E9 compared to V2 and V9 where Ce was normal, seem to indicate that in reaction with EDTA Ce is retained by clays much more strongly than the other RE. Thus the normality of Ce in A2-A4 may be an artifact and cannot be relied on.

3) The RE that had been in the fine carbonate which was dissolved by HCl + EDTA to obtain the clay probably became partly adsorbed on the latter; this part was 2% of the RE in solution according to the preliminary tracer experiment, but an unmonitored amount in the actual sample. If the RE were comparable in abundance and different in pattern from those in the clay, they might have modified the pattern of the latter. Judging from the RE abundances in the globigerina tests this is unlikely to be a

large effect, but such a judgment is admittedly only an extrapolation since no information is available on RE in the fine carbonate.

4) If ferromanganese minerals are not wholly soluble in EDTA under the given experimental conditions of temperature and time of contact and if these were present (e.g. as a coating on the shells - cf. Turekian, 1963 - or as discrete particles), the RE in the part undissolved by the EDTA would be included in the results for A1-A4 modifying and possibly obscuring the detrital RE pattern.

At present there is no way to estimate the relative magnitudes of the effects of these conceivable processes and their possible contributions to the determined RE values of samples A1 to A4. The observations on and inferences from the chondrite-normalized plots of the RE abundances in these samples are therefore subject to re-evaluation in the light of future studies on these processes.

The observations and inferences are as follows (see fig.4):

1) The absolute abundances of the RE in A1 to A4 fall into quite a narrow range: within  $\pm 20\%$  of their average, except Pr and Ce for which the ranges are  $\pm 25\%$  and  $\pm 30\%$ , respectively. This range is much narrower than that in the sediments from which Haskin and Gehl (1962) derived their "average sediment" distributions.

2) The chondrite-normalized heavy RE distributions of each sample fall very smoothly onto a close to horizontal line, especially those in A1 and A3 where this line extends from Tb through Lu (except Ho in A3). In A2 and especially in A4 a slight fractionation of this group seems to exist. One is tempted to relate the greater resemblance of this part in A1 and A3 to their closer K-Ar ages, 240 and 233 million years, respectively, as opposed to those of A2 (323 million years) and A4 (163 million years). Yttrium is "normal", i.e. it is on the same smooth line as the other heavy RE except in A4.

These features of the heavy RE and Y in the A1, A2, A3 clays resemble strongly the pattern in the North American shale composite plotted in fig. 4, bottom. (Tb looks enriched in the latter, but there seems to be a bias toward high Tb values in many of Haskin's group's analyses.)

3) The overall distribution curves of A2, A3, A4 with their rather strong fractionation of the light RE (and "normal" Ce if it is not an artifact) also resemble that of the North American shale composite, but they are fractionated more strongly, especially A4; its fr. index is  $16 \pm 1$  vs.  $\sim 7$  in the shale and  $\sim 8$  in A3. (In A2 it is indeterminate because of the missing La value, but it should lie between 9 and 12).

4) Unlike the shale, Eu is depleted in these clays, the Eu point lying ~20% (in A3) to ~45% (in A4) below the smooth distribution line. (This line may perhaps be considered rather arbitrary, especially in absence of Gd values, but the Sm/Eu ratios, to which this criticism does not apply, are also 35% (in A3) to 90% (in A4) higher than in the shale.)

As mentioned in section 3.1, inspection of log scale plots of chondrite-normalized RE distributions of many sediments including one of Minami's shale composites and several of those from which Haskin derived his "average sediment" (1962), reveals a Eu depletion of 20% - 40% with respect to the line connecting the normalized values of Sm and Gd. Thus, the Eu depletion in A2 - A4 does not put them apart from terrestrial sediments; the Eu depletion in addition to the stronger RE fractionation than in the North American shale only show that they are not genetically related to this shale. In view of the location of the core at the equator such a conclusion is not a surprise but rather additional data in favor of the point of view that RE distributions in sediments are not all the same and that moreover, they can be used as indicators for or against hypotheses of genetic relationships among samples.

Similarly, the stronger RE fractionation and Eu depletion in A4 than in A2 and A3, as well as the 60% Y enrichment in A4 vs.

its normality in A1, A2, A3 are probably significant in confirming the different K-Ar age of A4 and indicate that its material came from a different terrestrial source than the other three samples.

#### 3.3.4b RE in globigerina tests from core A180-74

##### Comparison of the RE in the tests to RE in marine clays.

Differences between the RE patterns in marine clays and in the tests were expectable for the following reasons:

Genetically, the obvious difference between clays and any plankton tests is that the first have a significant terrigenous component, whereas plankton is all hydrogenous, i.e. its RE must have passed a stage when it was dissolved in sea-water or in the pore solution of the sediment, whether in ionic, complex organic or inorganic, or colloidal form. The two sea-water RE distributions available at present (fig. 10) differ from each other, but they both differ even more from the distributions in all materials with an appreciable terrigenous component (figs 1, 2, 4) including the suspended particles in sea-water (MPS, fig. 10). Also, the mechanism that incorporate the RE into the tests are most likely to be different from those operative in adsorption of RE onto clays.

Comparing the RE patterns in these tests (fig. 5) to those in the 12 marine samples discussed in 3.3.2 (figs. 1 and 2)

we see indeed some distinct differences:

1) The RE in the tests are more strongly fractionated; their fr. indices range from 7.5 to 10 whereas the 12 samples range from 5 to 6.5.

2) The test have a larger Ce deficiency (non-uniform)

3) The tests have a Y excess (except A4C)

4) The tests have an Sm deficiency giving rise to a break in the RE distribution curve

5) The tests have absolute RE concentrations about an order of magnitude lower than the clays.

Note. we do not compare the RE patterns in the tests to those in the clays (A1 to A4) that were associated with them because we believe they were largely stripped of their hydrogenous components and there could hardly be any relationship between the purely hydrogenous RE in the tests and purely detrital RE in the clay.

The enumerated differences can tentatively be explained as follows:

(1) and (4) The relatively low fr. ind. of the 12 marine samples was explained (3.3.2) as possibly due to preferential adsorption of the heavier RE Sm to Lu, with strongest preference for Sm, on the surface of marine clays. The same, it was suggested (Goldberg et al) occurs with marine authigenic minerals. This would explain the minimum in the RE patterns of the two seawaters (fig. 10) and the strong fractionation from La to Sm in

samples SW and OM. The high fr. ind. and Sm deficiency in the tests could represent the pattern of the RE dissolved in the sea-water that was in contact with the plankton.

(2) and (3) The Ce deficiency and Y excess also seem to be a reflection of sea-water RE composition, since in the sample of Pacific sea-water whose RE pattern is known Ce is depleted by a factor of 4.5 (no value was given for its Y), and in the sample of Atlantic sea-water analyzed in this work, Y is enriched by a factor of about 2 (no value of Ce was obtained). The "normality" of Ce in argillaceous marine sediments may well be the product of mutual cancelling of deficiencies and excesses in different components, as suggested in 3.3.2; the "normality" of Y in them may similarly be due to inner cancellation, or possibly the Y excess in sea-water (if it proves to be a common characteristic) is in a chemical form available to organisms but less adsorbable on clays.

Comparison of the RE in globigerina tests to other marine hydrogenous and organogenic materials. Concentrations of some trace elements vary quite widely even among similar organisms, and the concentration of others can be very uniform. An example of the first kind is uranium (Tatsumoto and Goldberg, 1959) which varies by two orders of magnitude from some Gastropoda (0.004 ppm) and is on the higher side in corals and oölites (3-5 ppm). An

example of the second kind is strontium (Turekian, 1964), which is fairly constant at 1200 ppm in a wide variety of calcareous tests. Hence RE content of the tests could not be predicted from previously, extremely scanty, information, nor can the present results serve for such predictions except for stating that so far the RE contents of calcareous organic materials seem to be variable rather than uniform.

Within the group of 5 samples analyzed in this work the range is quite narrow, and it coincides exactly with the range of RE in the limestones analyzed for RE so far, but is ~ 20 times higher than RE in a recent shell composite (at least 100 times higher than in a shell analyzed in this work, and 50-80 times higher than in two corals, all in fig. 7). Balashov and Khitrov (1961) determined the total RE in live Foraminifera and their value coincides with that in sample AlK. They found up to 7 times more RE in other live calcareous plankton. The method used by them for ashing the plankton samples calls for ~ 5 g  $\text{Na}_2\text{O}_2$  per less than 1 g of sample.  $\text{Na}_2\text{O}_2$  (like NaOH) cannot be purified from traces satisfactorily, and they do not mention any blank RE determinations. This casts a possible doubt on these results (unlike their results for sea-water where a different method was used), but if confirmed it would show a very simple sequence with no appreciable total RE changes: live plankton  $\longrightarrow$  buried tests  $\longrightarrow$  limestone.

Some results discussed in conjunction with the oölite and shell, below, indicate that the organic matter is much richer in RE than the carbonate mineral part of calcareous organisms and thus a higher RE content in whole live plankton than in tests only is not unlikely. As mentioned before, the tests are depleted in Ce (see fig. 5) up to ~35%.

Ce values are known for only one other purely calcareous material, a recent shell composite (fig. 7), where the given Ce value is enriched with respect to the other points but its lower limit of error ( $\pm 70\%$ ) extends well below them so that no definite comparison can be made. Another Ce value is known in one limestone (Graf, 1960), where it is normal, but limestones may well contain some ferromanganese (Ce-enriched) component. Hence at present no conclusion can be made as to the prevalence of a Ce-deficiency in calcareous organogenic materials.

The Y in the tests is enriched by over 50%. As mentioned before, it is similarly enriched in sea-water, but not in its suspended solids. A Y enrichment is found in many, though not all, biogenic materials for which the whole RE distribution is known. It is enriched in two phosphorites (fig. 2 and Schofield and Haskin, op. cit.) which have recently been shown most likely to be replacement products of carbonate ion by phosphate ion in marine calcareous materials (and their RE patterns would thus be

inherited from those materials) (Degens, 1965, after Ames, 1959; Bushinsky, 1964); it is also enriched in hickory leaves (Robinson et al., 1958), in a coal (Yershov, 1961), in a sword-fish bone, and in the body of a clam (this work, fig. 8). Y seems normal, however, in two coals, two corals and a sea-shell composite (Schofield and Haskin, op. cit.) In these analyses the chondrite-normalized patterns of the heavy RE are rather bouncy, so that Y normality in them is not certain. Of non-biogenic marine materials Y is enriched in an oölite (which usually has, however, a considerable biogenic component) and depleted in the Caryn Peak manganese nodule (this work, figs. 7 and 9). No Y values are reported for any of the other three nodules that have been analyzed for all RE. Y is normal in an Antarctic marble but enriched in a British Columbia limestone (Haskin and Gehl, 1962).

This listing indicates that Y exists in natural waters in a mixture of different chemical species and their relative uptake by different bio-species and other materials varies. The chemical form in which the Y excess exists in sea-water is undialyzable (see fig. 10) and organisms possibly incorporate RE mainly in this chemical form.

Intercomparison of the globigerina samples, and conclusions. The characteristic features of the five samples are:

1) The four samples of tests in the same size range ( $>75\mu$ ) are almost identical in absolute values and distribution of the individual RE. They vary only within 10% to 20% of their average, except for Pr and Ce which vary within 25% and 30% respectively, although the ages of the tests are about 25,000 years apart (by rough extrapolation of  $C^{14}$  age determinations made along the first meter of the core), and although the species composition varies, with warm-water forms predominating in A3C and A4C and cold-water forms predominating in the other samples.

2) The smaller size tests ( $25\mu - 75\mu$ ) have about 3.5 times higher RE, whose distribution is practically identical to that in the larger ones. These tests were defined by Dr. Cifelli of the Smithsonian Institute as immature, whole tests, not fragments of larger ones (personal communication).

The uniformity of RE content and composition indicates either:

a) that over a span of about 75,000 years the trace element composition in the euphotic layer of the water above that core was practically constant (assuming that the tests were a closed system to RE since their deposition), or

b) that the tests were open systems to RE and migration of the RE in the pore-solution was extensive enough to equalize the RE compositions in tests across at least 3 m of sediment depth,

by diagenesis and adsorption.

On the basis of present-day information on trace elements in deep-sea cores neither alternative can be given preference over the other. Migration in the sedimentary column has been demonstrated for  $U^{234}$ ,  $Th$  and  $Ra$ , and indicated for other elements. On the other hand, 80,000 years are geologically a short time and uniformity of sea-water composition over this time span is not unlikely.

The higher RE content of the small tests along with the similarity of their distribution can also be explained in one of two ways:

a) That these species, when young, adsorb more RE, whereas later in life they discriminate more strongly against them;

b) That a considerable part of the RE was adsorbed by the tests after death and the smaller tests adsorbed more due to their larger surface area per unit weight.

Post-depositional adsorption of RE is known to occur on fish-bones, which are quite low in RE when the fish are alive. (Arrhenius and Bonatti, 1964; Kochenov and Zinov'ev, 1960; Bloch, 1961). Increases can be as large as from 1 ppm to a few thousand ppm total RE. Likewise, Ba was found to be sorbed by dead organic matter. Another indirect corroboration for the possibility of

post-depositional adsorption can be seen in Turekian's (1964) results on various trace elements in a series of size fractions of  $\text{CaCO}_3$  ooze. High enrichments of Sr, Cu, Ni (and lesser of Pb and Sn) were found to co-vary with extreme enrichments of Mn in the  $< 10\mu$  size range, indicating coating by Mn hydroxides including coprecipitated elements. In this case the small grains were broken fragments of the large ones, so the selective enrichment must have occurred after death. While this proves the existence of post-depositional Mn coating in general (unless the clay was not removed - no details on its removal are given - since in such a case the enrichment may have been all in the clay or in a separate Mn-Fe-hydroxide phase in the same size range), it is of particular relevance to the 3.5-fold enrichment in the size ranges analyzed in this work that Turekian found Cu and Ni in the  $25\mu - 75\mu$  range to be 3-10 times higher than in the  $> 75\mu$  range, in both of which there is no clay; they may have become adsorbed on the tests directly, or coprecipitated with Fe hydroxide (since Mn was not enriched and Fe was not determined in that study, the latter is mere conjecture).

Krinsley and Bieri (1959) studied fresh and sedimental pteropods and found that their aluminum content increased strongly after deposition to a widely variable extent. Copper was gained by them in some cases but not in others, and Mg, they found, could move both in and out of gastropod shells during diagenesis without

recrystallization of the shell material.

Post-depositional adsorption on calcareous tests is thus well established for other trace elements. To establish its existence specifically for RE more tests of live calcareous plankton (excluding the soft body parts) must be analyzed, and RE analyses of many more than two different size fractions from a single core sample must be done.

In summary:

(1) The analyzed tests of similar size range are very uniform in their RE: they differ noticeably in RE distribution and absolute value from marine sediments where clay predominates.

(2) Though not identical to either of the two sea-water RE patterns determined so far, the tests and the sea-water patterns deviate from the (rather uniform) marine clay RE patterns in the same direction as the sea-water: the angle pattern due to Sm and neighboring elements depletion, Ce depletion, and Y enrichment.

(3) The higher RE content with identical distribution in the smaller tests is quite probably related to their larger surface area and would point to post-depositional adsorption of RE, or of RE incorporated in an iron hydroxide phase.

(4) The RE values in the tests coincide with reported RE values for limestones, possibly explaining the latter. RE values in larger calcareous objects, shells and corals, are 20

to 100 times lower. (However, even in the lowest reported RE content the RE/Ca ratio is ~100 times higher than in Pacific surface water). RE values in live plankton similar to or higher than in our samples have been reported, but cannot be accepted as final without additional confirmation.

3.3.5 Cariaco Trench Sediment  
(Table 4, fig. 6)

Sample description. This is a sample of the bottom surface mud near the center of the Trench, close to its Western steep slope. Water depth at sampling site 1317 m; maximum depth in the Trench is < 1500 m. The sample contained 30% water, and was largely calcareous.

Discussion. The total RE content of this sediment (> 100 ppm) is intermediate between that of the pure foram tests and that of clays, as would be expected from its being a mixture of clay and calcareous material. It is close to that of some of the mixed marine samples analyzed by Wildeman and Haskin, (op. cit.).

Its RE distribution, however, is distinctly more fractionated (index ~10.5) than our pelagic clay samples (index 5.7 to 5.9) and Haskin's various pelagic samples (index 5 to 6.5). It lies close to the range of the RE fr. ind. in the tests (7.5 to 10), but differs from them in its Ce and Y being normal. It

resembles most strongly another non-pelagic calcareous sediment from Florida Bay (fig. 6). The similarity is quite pronounced for the elements La through Tb. The heavier elements in that sample give a very unusual pattern which seems to call for additional confirmation.

The Black Sea sediment average by Ostroumov is given in the same graph since the Black Sea resembles a trench environment in the stagnating nature of its deeper waters which result in both cases in enrichment of unoxidized organic material and a low Eh. Although only values from La through Dy are available, a trend of heavy RE depletion is apparent, making it distinctly different from the group of 12 pelagic sediments discussed earlier, in all of which the heavy RE content is relatively much higher.

A tentative explanation of the relative heavy RE depletion in the Trench sample and the Black Sea samples (leaving out the Florida Bay sample because of its very unusual RE distribution) may be that the high organic and  $\text{HCO}_3^-$  ion content of the stagnant waters preferentially complexes and keeps in solution the heavier RE, leaving the sediments relatively enriched in the lighter RE with an overall strongly fractionated RE pattern.

### 3.3.6 Oölite

(Table 4, fig.7)

Sample description. Well developed rounded (but pitted) oölite from the Great Bahama bank, grain size mostly in the range 0.3 - 0.8 mm, less than 20% non-spherical; less than 5% obvious shell fragments.

Discussion. In an attempt to dissolve off only some outer layers (the inorganically precipitated part - Newell et al., 1960) of the oölite, Ce and Y tracers were added at the beginning of the dissolution and about 5% of the oölite was dissolved in 1N HCl. The tracer yields in the dissolved part were only 15% Ce and 21.5% Y showing that the major part of the RE from the dissolved part would be sorbed by the undissolved oölite, presumably because of the high pH on its surface.

In the course of the work done to determine the yield in the solution it was revealed that the tracers (and by inference all the RE), would not coprecipitate with ferric hydroxide, indicating that an organic complexing agent was present and kept them in solution. After evaporating this solution with HClO<sub>4</sub> the RE coprecipitated readily and completely with ferric hydroxide as usual.

These experiments showed that meaningful undistorted RE values could readily be obtained only on the whole oörites including the organogenic cores of the grains which we had wanted to

exclude.

The RE content in the oölite is about an order of magnitude lower than in the >75% foram tests (~ 2 ppm total RE vs. > 20 ppm), limestones and recent calcareous sediment, and the RE pattern is markedly different - fr. index 3 to 3.5 (some La, probably no more than 25%, was lost in the elution, hence the uncertainty in fr. index) vs. 7.5 to 10 in the tests and limestones, i.e. the oölite is relatively up to 3 times richer in the heaviest RE. Like in the tests, however, Y is selectively enriched (by 60% or 100%; compared to the Ho value or the Tm-Yb-Lu line respectively).

Its low RE content and low fractionation index are very close to those found by Schofield and Haskin (op. cit.) in a recent sea-shells composite collected at random on a New Jersey sea-shore (fig. 7), except that in the latter Y is normal. Roughly similar RE contents and distribution were found by the same authors in a recent and a Pleistocene coral in Florida Bay (fig. 7).

Five out of seven carbonate rock composites analyzed for RE by Balashov et al. (1964) also had comparably high relative heavy RE contents, (in one the RE composition was not determined and in one deposited in an arid climate, there was no such pronounced heavy RE enrichment). The absolute RE contents in these

were in the range of those previously reported for limestones:  
28 to 160 ppm.

An experiment carried out by the same authors on two almost pure carbonates (98% and 98.5% soluble in 10% HCl) indicates that the high heavy RE content in carbonates may be all in the acid-insoluble organic part of the calcareous material. They determined separately the RE in the soluble and insoluble parts, of the two samples, and found  $\frac{\sum \text{Ce}}{\sum \text{Y}} = 6.3$  in the soluble parts of one and 4.0 in that of the other, whereas the corresponding ratios in the insoluble parts were ~2 and 1.3. Then they ignited an additional amount of the first sample and proceeded as before. The  $\frac{\sum \text{Ce}}{\sum \text{Y}}$  ratios in the ignited samples were 1.8 in the soluble part and ~4 in the insoluble. About  $\frac{1}{2}$  out of the 2% insoluble became soluble following the ignition, and was hence presumably organic. The RE content of the (unignited) soluble part was 28 ppm, of the (ignited) insoluble 365 ppm, and of the part solubilized by ignition 465 ppm, but the latter seems to have contained, or adsorbed during the dissolution of the (unignited) soluble part, a major part of the total heavy RE of the sample.

In view of this it is not impossible that the rather high fractionation found in the foram tests in this work may have been an artifact caused by centrifuging out the insoluble fraction which included the organic material originally present in the tests,

and which also may have contained high heavy RE values. Thus the RE distribution in the tests cannot at present disprove the assumption that a RE pattern relatively enriched in the heavy RE is characteristic of calcareous marine material. This includes the oölites, which are known to contain a sizeable organic core. The relatively low heavy RE found by Haskin's group in 2 limestones and by Graf (1960) in one limestone may be largely due to some clay content. As shown before, clays contain 10-15 times more RE than calcareous material, and thus ~10% clay in a calcareous sample will dominate the whole-sample RE pattern.

The similarities in RE content and distribution between the oölite, the shells and the corals compared to the 10 times higher RE content in calcareous plankton tests of  $>75\mu$  size and even higher RE in smaller,  $25\mu - 75\mu$  size tests, could mean either that the larger forms actually take up less RE, or that the smaller ones, due to their large surface area, got much of the RE by external adsorption rather than by metabolic uptake. This attempt at interpretation is merely speculative due to the scarcity of RE data on pure recent living forms and the known variation of the same trace element contents even between different species of the same family, mentioned in 3.3.4b.

The uranium content of oölites and corals is very similar (as is the case for RE), around 3 ppm (range from  $<2$  to  $>5$  ppm), in contrast to calcareous plankton which Tatsumoto and

Goldberg (1959) found to range from 0.01 to 0.5 ppm. Since  $\text{CaCO}_3$  precipitated from sea-water by  $\text{CO}_2$  in the laboratory also contains about 3 ppm U, this was seen as a support to the argument that oölites are inorganically precipitated in the sea. (In view of the similar U content in corals this support seems tenuous). The similarities in RE content and pattern between the oölite, shells and corals, as well as absence of information on inorganic coprecipitation of RE with  $\text{CaCO}_3$  in sea-water medium, make the oölite RE results unsuitable as evidence for or against the argument of inorganic origin of the outer layers of oölites. These layers may well contain 10 to 100 times less RE than the admittedly organogenic "nucleus" and in this case our RE results would represent practically only this organogenic part which is usually either a broken shell fragment or a faecal pellet (Newell et al, 1960). Our preliminary experiments showed that to analyze for RE in the outer layers alone they must be ground off mechanically.

As a final note, the U contents of corals and oölites quoted above account for the anomalously high Ce and Nd values in our oölite and Schofield and Haskin's coral. The anomalies are quite obviously slow-neutron fission products of the uranium in these materials. No measures for removal of U from our oölite sample were undertaken, since much higher RE values had been expected.

### 3.3.7 Shell of Polynices Heros

Description. A fresh undamaged recent shell of Polynices Heros, a snail that lives partly burrowed into the mud in very shallow sea-water. The empty shell was collected on the Boston sea-shore in 1961.

Discussion. The sample was irradiated for 1 hour and therefore all RE elements except La, Sm and Eu were below detection limit with the equipment then at hand. The standard RE mixture irradiated along with this sample was lost in the post-irradiational procedure and a different standard was used to calculate the amounts of La, Sm and Eu. The likely error thus introduced is  $\pm 10\%$  and certainly does not exceed  $\pm 50\%$ .

The La, Sm and Eu contents of this sample,  $< 0.033$ ,  $< 0.004$  and  $< 0.001$  ppm respectively, are the lowest found so far in any material except natural waters, and even these values are only upper limits since they include undetermined reagent blank values. Therefore, they are of interest in spite of the inaccuracies due to the loss of corresponding standard and lack of blanks. They are an order of magnitude lower than the corresponding values found by Schofield and Haskin in their sea-shell composite in which whole shell samples (i.e. including their organic components) were analyzed. This may indicate that the pure carbonate crystals

in shells, which comprise 95% to 99% of the shell material, contain 2-3 orders of magnitude less RE than the organic network in it. An analogous situation was found for Zn (Crocket, 1960).

The fact that the La, Sm, and Eu contents of our Globigerina test samples from which the organic insoluble part had also been excluded, were 100 times higher does not necessarily contradict this hypothesis, since it is likely that soluble RE have been added to them after death and deposition, in one or several ways discussed above. Also, decay of the organic part of the shell probably solubilizes the RE of the originally insoluble organo-metallic compounds of the shell framework, and they too become internally adsorbed on the carbonate microcrystals.

Assuming that the shell consisted of pure  $\text{CaCO}_3$ , the three RE/Ca ratios in it would be less than 10 times higher than in the sea-water analyzed for RE by Schmitt and Smith (op.cit.) assuming 400 ppm Ca in the latter. If indeed the RE content of the organic part is higher, it must be incorporated there by a metabolic process quite distinct from that which secretes the carbonates of the shell.

3.3.8 Body of Quahog clam  
(Table 4, fig. 8)

The lighter RE concentrations in the wet weight of the clam are almost twice higher than the upper limit concentrations in

the Polynices Heros shell. On a dry weight basis La is about 4 times higher than in the recent shell composite (fig.7), but this ratio decreases steeply along the RE line.

The RE pattern found in the body of the clam has no parallel among non-igneous RE patterns known to date. It is extremely strongly fractionated throughout the whole group, with a fractionation index of 75 ( $\pm 20$ ). The highest fr. index known to date in sedimentary rock and organogenic or organic materials is less than 20. Among igneous rocks only nepheline syenites, some granites and one carbonatite (see below) have fractionation indices of comparable magnitude - between 50 and 100. Its uniqueness lies especially in the fractionation of the heavy RE, which are here fractionated about as strongly as the light RE, resulting in a chondrite-normalized curve which is roughly straight and does not have the inflection point beyond which the remaining chondrite-normalized heavy RE values characteristically lie on a line close to horizontal. This low fractionation of the heaviest RE occurs even in the igneous materials mentioned above in which the RE from La to the inflection point are fractionated even more strongly than in the clam. Among non-igneous materials the strong fractionation of La through Sm is paralleled in the Pacific sea-water (fig. 10) and the sword-fish bone (fig. 8), but in both these the normalized RE curve turns up at the heavy RE end, i.e. the heaviest RE are gradually enriched

in comparison to chondrites, whereas in the clam the strong gradient depletion continues down to Lu.

It is interesting to note (see fig. 8) that Y is enriched relative to the Tb-Lu line like in many organogenic materials and in the Atlantic sea-water but Ce is normal in spite of its strong depletion in the Pacific sea-water (see discussion of these Y enrichments in comparison to Y enrichment in the tests, section 3.5.2). The RE enrichment factor in the clam over the Pacific sea-water is  $\sim 10^4$ , whereas that of Ca is only about 1.5.

This RE analysis of the clam is the only fairly complete set of data on the RE in the soft body parts of a living organism and extensive interpretation is therefore quite premature, especially since the RE pattern in the sea water in which the clam lived is unknown. If a similar RE-pattern is found in the latter, the pattern in the clam would be a straight forward result. If, however, it is different, then either a strikingly potent selection mechanism is operative in the clam, or it represents the RE pattern that exists in the sea in a form available to the clam, presumably the part that exists as simple ions in true solution. Our RE analyses of sea-water and the undialyzable fraction of sea-water (see below), although not accurate enough for anything but tentative conclusions, seem to point to

just this type of distribution of the heavy RE occurring in the sea in a dialyzable ionic form.

At first sight this highly fractionated pattern seems quite incompatible with the characteristically low fractionation index found in whole shells, corals and the oölite, and its attribution to the organic material in them, strengthened by the results of Balashov et al.(op. cit.) on ignited vs. non-ignited carbonate material (see above). The last mentioned result is actually different in nature, since the extreme preferential uptake of the heavy RE by the organic material may well have occurred after dissolution of the sample rather than when it was part of a living organism. The relatively high heavy RE content of the shell composites, however, if found to exist in the Quahog clam shell as well, could only be explained by assuming either that the different RE forms in the sea are differently utilizable to different metabolic cycles in the clam, or that fractionation of ingested RE occurs inside the clam, the shell network tissues concentrating preferentially the heavy RE and the body tissues doing the opposite. Either possibility should be of great interest to physiologists and biochemists as well as geochemists. Extensive work on RE patterns in the animal world is clearly called for and seems to promise very interesting results.

3.3.9 Bone of Sword-Fish  
(Table 4, fig. 8)

The sample was irradiated for two hours, which gave inadequate sensitivity.

The RE concentrations in the bone are very close to those in the clam on the wet weight basis, except for Yb and Lu which are respectively 4 and 10 times higher than in the clam. Thus the chondrite-normalized curve rises beyond Ho or, at least, stops falling.

The small sample and relatively short irradiation, picked according to expectation of much higher RE concentrations, resulted in too low sensitivity for four of the RE and high uncertainties for the others, so that pattern interpretation is very tentative. However, the sharp slope of the chondrite-normalized pattern from La to Dy is even within its wide limits of error very different from most other materials and is given additional credibility by its similarity to that of the clam. The limits of error of the Ho, Yb and Lu values are such that the real slope may be anywhere from zero to highly positive, but it is certainly unlike the negative one of the clam.

Previous analyses for RE in fish-bones among others compiled by Vinogradov (1944), showed only 0.00% total RE, i.e. <100 ppm; this analysis shows that total RE in the hard

part of fish-bone can be as low as 0.8 ppm. On a dry basis the RE concentration in the clam is about 10 times higher than in the fish-bone. The very high concentrations of RE (up to >1000 ppm) found by Kochenov and Zinov'ev (1960) and by Arrhenius (1964) in fossil fish-bones and shown by the latter to accrete when the bones undergo partial dissolution by lowered pH, are thus all the more striking.

The problem of fallout Ce, as well as the interesting RE patterns found here, call for many more RE analyses on different body parts of different fish.

3.3.10 Manganese nodule  
(Table 4, fig. 9)

The outstanding feature of this nodule, like of other nodules analyzed before, is the selective Ce enrichment. The enrichment factor over the smooth line of the other (chondrite-normalized) RE in it is  $3 \pm 0.75$ . In the nodule reported on by Goldberg et al. (1963) this enrichment factor is 1.6 and in Pachadzhyanov's (1963) no. 4555, it is 7; i.e. this factor is variable. (No estimates of error are given by either author; the RE were determined by X-ray fluorescence in both works). The chondrite-normalized RE pattern in the second nodule reported by Pachadzhyanov is so extremely jagged that the quality of the analysis seems questionable. However, though no meaningful

enrichment factors for Ce can be estimated here, Ce stands higher than all other RE elements. The selective enrichment of Ce over other RE in nodules was noticed even before complete RE analyses became available, and Goldberg (1961) suggested that it was due to incorporation of Ce into the  $MnO_2$  lattice layers as  $CeO_2$ . He suggested further (1963) that the selective enrichment of Ce in the ferromanganese minerals is responsible for the 6-fold Ce depletion (relative to the adjacent RE) in sea-water.

It should be noted that under Eh conditions prevalent on the ocean bottom, where nodules accrete, their immediate environment probably has a higher Eh than the water and other sediments ( $Eh = +0.4v$  measured in the latter, and  $+0.54v$  calculated for a mole fraction of 0.2  $MnO_2$  at equilibrium with  $10^{-9}M Mn^{+2}$ ) and this would indeed make them a concentration site for  $CeO_2$  which has an extremely small solubility product (probably smaller than  $10^{-47.7}$ , the S.P. of  $Ce(OH)_4$ ). However, farther above the bottom higher Eh values are common; the Eh of water saturated with oxygen and at equilibrium with it is  $+0.75v$ . At this Eh the concentration of  $Ce^{+3}$  at equilibrium with pure  $Ce(OH)_4$  would be  $10^{-14}M$ , whereas the "normal" Ce concentration in the Pacific sea-water reported by Goldberg would be  $10^{-13}M$ . Clearly, under these conditions Ce could become depleted even by pure  $Ce(+4)$  hydroxide precipitation. (The  $RE(OH)_3$  solubility products

are about  $10^{20}$  times higher and could not be exceeded with the prevalent sea-water  $\text{OH}^-$  and RE concentrations). Between these two extremes of Eh occurring in sea-water all intermediate values can exist, of course, and at any Eh +0.4v and higher any material that can adsorb  $\text{Ce}(\text{OH})_4$  or  $\text{CeO}_2$  in dispersed low concentration solid solution form can reduce the Ce content of the sea water below the "normal"  $10^{-13}\text{M}$ , bringing it down lower the higher the Eh.

The large bulk of clays (a likely carrier for the Ce) in the ocean could carry it without becoming noticeably enriched in it.

In the light of these considerations, Pachadzhanyov's (1963) suggestion as to the source of the excess Ce in nodules should be mentioned. He notes that the elements most highly enriched in the nodules relative to shales and pelagic clays, i.e. Mn, Co, Ni, Ce, V, and the Nb/Ta ratio, all have variable valences, and they are all more soluble in lower than in higher valence states. Since in the upper layers of pelagic sediments just after burial the Eh values drop (because of organic decomposition and scarcity of oxygen supply) and range down to -0.2v, he suggested that appreciable amounts of the above elements pass there into the pore solution and, because of the concentration gradient thus established, they diffuse upward

into the sea-water. There they precipitate again, a large part of them accreting into ferromanganese nodules.

Neither he nor Goldberg offers a mechanism that would account for the concentration of the other RE in nodules. The concentrations of RE in nodules are relatively so high and in sea-water so low, that precipitation of  $\text{RE}(\text{OH})_3$  (in solid solution, of course) is impossible - their solubility products are much too high. For example, the dissolved La concentration in sea-water would have to be an impossible 10M to precipitate a mole fraction of  $x \sim 10^{-4}$  of  $\text{La}(\text{OH})_3$  in a nodule, since the solubility product of this compound is about  $10^{-13}$ . (The RE are relatively strong bases!) However, we know from tracer experiments that flocculating ferric hydroxide is a superefficient scavenger for RE: e.g. 5 mg of it per liter sea-water carry down > 95% of the RE in it, without any appreciable fractionation, and at higher RE concentrations it is even more efficient. Thus all RE including a "normal" relative amount of Ce are probably incorporated in the nodule by its ferric hydroxide component, whereas an additional amount of Ce is taken in due to the extremely low solubility of  $\text{CeO}_2$ , possibly indeed into the  $\text{MnO}_2$  lattice, the latter ensuring a local Eh higher than that of the surrounding bottom water and thus promoting  $\text{CeO}_2$  formation.

Pachadzhyanov's suggestion of upward migration of elements from buried sediments due to their solubilization by the low Eh could not apply directly to RE other than Ce, but if an independent ferric hydroxide phase were part of them and dissolved due to the low Eh, any RE originally coprecipitated in it would get released into the pore solution. Part of them as well as part of the Ce would probably get readsorbed on the sediment, but some part might possibly reach the sea-water. RE analyses of pore solutions in the reduced layer are needed to confirm the existence of such a mechanism. The well established increase of RE concentrations in sea-water with depth would be easiest to explain by this mechanism.

Much evidence has by now been presented for submarine volcanic origin of much of the manganese oxide in many nodules (quoted in Arrhenius and Bonatti, 1964), and in these cases, presumably, the RE and other elements found in the nodule have the same origin.

The overall distribution of RE in the nodules analyzed is seen from the graph to vary rather widely with fractionation indices from 10 to 1 and curve shapes ranging from the rather unusual convex-up in Goldberg's Horizon nodule, to almost straight in Pachadzhyanov's no. 4555, to wavy but largely concave-up (as in most terrestrial materials) in our Caryn Peak nodule. Additional studies on these nodules might possibly reveal a relationship

between the RE patterns and the volcanogenic vs. terrigenous origin of the nodule constituents. No selective Sm enrichment is apparent in any nodule except Goldberg's, including three nodules analyzed only for La, Sm, and Eu by Kawashima et al. (1961).

No Y values are reported for the three nodules analyzed for all RE. In our Caryn Peak nodule the Y is depleted by about one third compared to the other heavy RE. In view of the established absence of fractionation of Y from other RE during the ferric hydroxide scavenging of RE from sea-water and the relative enrichment of Y in our sea-water no explanation of this depletion can be given at present.

3.3.11 Atlantic deep sea-water fractions  
(Table 5, fig. 10)

The method of obtaining the different fractions has been described in section 2.1.3. In view of large uncertainties of many of the RE values (due mainly to large blank uncertainties - see Appendix C), the discussion of the results is limited to pointing out only some facts which seem fairly well substantiated. No generalized implications and comparisons with RE distributions in other marine materials are deemed warranted before additional data are collected.

1) The RE concentrations found in this work in deep Atlantic sea-water coincide rather closely with the values reported by Goldberg et al. (1963) for deep Pacific sea-water except for La and Pr, but they seem to differ somewhat in distribution (see fig. 10).

2) The  $>0.45\mu$  particulate phase (MPS) contained about half or more of each RE of the total sea water sampled (total = SW + MPS). Similar results were obtained by Balashov and Khitrov (1961); in nuclear fall-out studies by Goldberg et al. (1960), and by J. Carpenter in Ce adsorption studies (personal communication, 1963). In spite of the large errors in the values obtained for many elements the RE distributions in this phase and in its associated filtrate differ certainly in at least two features: (a) the normalized Sm and Eu values are distinctly higher than the heavy RE in the solids, but in the filtrate they are lower or the same; (b) the normalized Y is in line with the other heavy RE in the solids, but distinctly above them (by about a factor of 2) in the filtrate. These differences have some interesting implications.

3) The undialyzable part of the  $<0.45\mu$  filtrate of 700 m (OM) contains about  $1/3$  as much RE as the total  $<0.45\mu$  filtrate of 1100 m (SW). Since the total RE content of sea-water increases with depth (Balashov and Khitrov, op. cit., Goldberg, op. cit.), it may have constituted up to  $1/2$  of the RE in the  $<0.45\mu$

filtrate from which it was dialyzed out. The undialyzable fraction comprised presumably particulate matter  $<0.45\mu$  down to colloidal size, since the membrane pore width was  $20 \text{ \AA}$ , and organic complexes of Mol. Wt.  $\geq 1000$ . It is impossible to tell at present which of these is more important, but the two forms together appear quite important as RE-carriers in the sea.

4) The distribution of RE in OM and in SW is generally similar; Y is enriched in both. However, the Ce/Nd ratio (see Table 5) is considerably higher in OM than in SW, indicating a larger relative Ce content in OM. This is in line with Carpenter's result of finding 97% of the total  $\text{Ce}^{144}$  (which he had added) on top of a  $10\mu$  filter. (His  $0.45\mu$  filter retained ~60% of the Ce activity). It seems to indicate that the Ce in the sea is practically wholly associated with particulate matter, whereas Y is perhaps preferentially organically complexed in complexes of various sizes.

5) The Y enrichment in the filtrate and undialyzable vs. its "normality" in the  $>0.45\mu$  phase should throw light on comparable occurrences in other samples. Y is "normal" in all the 12 marine samples (discussed in 3.3.2). Since the suspended solid phase is a direct precursor of marine clays (it is marine clay in "statu nascendi"), this presents a coherent sequence of events. We believe that the  $\leq 25\%$  RE which apparently exists

in the sea in true solution (dialyzable form), is in dynamic equilibrium with the surface adsorbed RE in the particulate phase; the excess of Y in the 40.45% filtrate would simply indicate that the character of the Y-holding species in the sea is such that its excess in the filtrate is in equilibrium with the normal Y on the particle surfaces. Thus the marine clays can remain indefinitely with a "normal" Y content. It would be very interesting to find what is the excess-Y-holding species.

The statement regarding dynamic RE equilibrium between the solid surfaces and the solution is based on two experimental observations: (a) our own and other tracer studies indicated that RE adsorption and desorption from the particulate phase surface occurs very readily; (b) Balashov and Khitrov found that the particulate phase contains about 50% of the total RE at all depths, although the total RE content increases with depth whereas the particulate phase content stays constant at all depths. This would mean that these surfaces are not saturated with RE but that when they contain about 50% of the total RE in the system they are at equilibrium with the RE in solution.

Note. Since the amount of suspension is so small and its RE content is relatively so high, the group separation of RE from sea-water should be done with special attention to this invisible constituent. The suspension is almost certainly co-

precipitated with the  $\text{Fe}(\text{OH})_3$  or other RE-scavenging precipitate, but since it is largely silicate (clay) it is not at all certain that it dissolves completely in the HCl used to dissolve the precipitate. Unless this precipitate is treated with  $\text{HF} + \text{HClO}_4$  the RE values obtained most probably represent the dissolved RE plus a variable fraction of the RE in the suspension.

3.3.12 Alnö Carbonatite  
(Table 4, fig. 11)

The igneous origin of carbonatites has gained wide acceptance only in very recent years, one of the most convincing proofs having been given by  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio measurements <sup>et al.</sup> by Powell (1965) who found very significant differences in this ratio between carbonatites and sedimentary carbonates. This carbonatite sample was analyzed for RE to see whether comparably large differences existed between its RE pattern and that of sedimentary carbonates, in addition to the well known difference in RE content (RE are highly enriched in carbonatites).

Comparison of the absolute values shows that the RE content in this carbonatite is from about 100 to 10 times (for La and Tm respectively) higher than in the globigerina tests. Comparison of the distributions (see figs. 11,5) seems to preclude any genetic relationship between sedimentary carbonates and carbonatites, since both the very strong fractionation (fr. index

~60) and the almost straight-line chondrite-normalized pattern from La through Ho have been found so far only in nepheline syenites (Goldschmidt, op. cit., Sahama, op. cit.) and other alkalic rocks, and in a few granites, among them G-1 (Towell et al., 1965). (In granites, however, Eu is usually depleted (Chase et al., 1963), whereas in the carbonatite it is normal).

The two carbonatites analyzed by Schofield and Haskin have lower RE contents and much weaker fractionation, but their straight-line chondrite-normalized pattern with Eu normal likens them to the Alnø carbonatite and to other igneous rocks, and distinguishes all the carbonatites from the characteristically concave-up sedimentary RE pattern with Eu somewhat depleted. Ce in the carbonatites is variably below or above normal. The characteristically igneous RE pattern is an additional, though by now perhaps hardly needed argument in favor of igneous origin of carbonatites in the old and die-hard controversy about them.

#### 3.4 Concluding Remarks

This survey of RE distributions in the marine environment has revealed variations that indicate the scope and interest in the study of the geochemistry of RE in the sedimentary cycle in general and in the marine environment in particular. They also show that the existing data are insufficient for meaningful generalizations.

In the majority of the limited number of whole-core samples analyzed for the complete RE group so far the RE distributions were rather uniform, but they represent the result of mixing of components the RE distributions of which may vary quite widely. To understand the geochemistry of the RE in this environment attention must be focused on the RE in the components rather than in their accidental mixtures.

Information on behavior of RE in the marine environment revealed or indicated in this study includes the following. More than half the RE content of marine clay is apparently adsorbed on the clay surfaces, and the distribution of the adsorbed RE can be quite different or quite similar to that in the interior. The RE content in calcareous parts of organisms varies over more than an order of magnitude and the possibility was indicated that in fresh calcareous structures their larger part occurs in the organic components and in sedimented old calcareous material a great part of the RE content is post-depositionally adsorbed. RE distributions in live organic matter appear to differ greatly from those in old organic remains. Many materials of organic origin are selectively enriched in yttrium relative to the other heavy RE. The RE distribution in solids ( $> 0.45\mu$ ) suspended in sea-water differs noticeably from that in the water. A considerable part of the RE in filtered sea-water occurs in an undialyzable

-135-136-

form. The RE content and abundance pattern in the analyzed oolite are very different from those in the globigerina tests. The manganese nodule analyzed is selectively depleted in yttrium and enriched in cerium. The four complete nodule RE patterns now known vary in slope and/or curvature.

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PART II

## APPENDIX A

### A REVIEW OF SOME ADDITIONAL LITERATURE

In the presented survey and discussion of the rare earth distributions in the marine environment, the pertinent limited literature data available have been used extensively for comparison with and as a complement to the data obtained in this work. However, two papers by Balashov and coworkers, one dealing with total RE contents of sea-water constituents but not with distributions of the individual RE, and the other with sedimentary rocks which are at present in a terrestrial, not marine, environment, offered less opportunity for direct comparisons and quotations in the body of the paper, yet it is of interest to review them in more detail.

Balashov and Khitrov (1961) determined colorimetrically the total RE (including Y) in 21 samples of unfiltered sea-water from nine sites in the Indian Ocean. At three sites only surface water was sampled, four sites were sampled at two depths each and two sites were sampled at four and five depths respectively, one at 0, 100, 1000 and 2600m. and the other at 0, 50, 200, 1870m and at the bottom. They used  $Ce^{144}$  for determination of the chemical yield of the group separation procedure, and estimated their analytical accuracy to be  $\pm 20\%$ .

In pelagic waters (17 samples) the concentration ranged from  $0.85 \mu\text{g/l}$  to  $3.8 \mu\text{g/l}$  total RE, increasing with depth in all except two samples, but with no noticeable quantitative relationship between the concentration and the depth. In two surface samples of rather shallow near-shore waters the RE concentrations were two and three times higher than in surface samples of pelagic waters: about  $2 \mu\text{g/l}$  RE on the surface of 95m-deep water on the Indian shelf ( $3.8 \mu\text{g/l}$  at 90m depth at the same site), and  $2.8 \mu\text{g/l}$  RE on the surface of 40m-deep water in Colombo Bay. The highest total RE concentration,  $4.0 \mu\text{g/l}$ , was found at the surface of 1020m-deep water over the continental slope of India, about  $0.8^\circ$  south of the Indian shelf sample. The authors do not comment on this sample; they only generalize that the RE content increases with proximity to the shore. The solid suspension ( $>0.7\mu$ ) of this particular sample was also analyzed for RE; it contained only  $0.8 \mu\text{g}$  RE per liter water, hence the exceptionally high RE value in this water was either in some soluble form or associated with particles finer than  $0.7\mu$  and no ready explanation for the singularly high RE content is apparent.

The suspended particles larger than  $0.7\mu$  filtered out of four samples of a single water profile, 0m to 2600m, were also analyzed for RE. No RE were found in the surface sample, and in the three other samples the RE content of the suspension was roughly half the total RE content of the unfiltered sea-water, although the total

amount of suspension remained roughly constant at all depths. The RE concentrations in the three suspensions were 280 ppm, 430 ppm and 1400 ppm respectively. The results in these three samples are the basis of the authors' generalization that about half the RE in sea-water is associated with solids. The solids apparently adsorb RE as they sink to greater depths, keeping up a rough equilibrium with the higher dissolved RE content in the surrounding water, and are probably the main agent of RE transport from the surface to deeper waters and to sediments. It seems necessary to comment that particles smaller than  $0.7\mu$  could contain a very appreciable part of the remaining RE, due to their larger specific surface area, since the quoted data indicate that much or most of the RE of the  $>0.7\mu$  particles are surface-bound. The state of the 50% of the RE which are not in the  $>0.7\mu$  particles remains largely unknown.

The authors also determined the RE content in three samples of copepods filtered out by a net towed at 0-100m water depth, in one sample of non-motile plankton (mainly *Pyrocypis*) and in one sample of foraminifera. The copepods ranged from 200 to 420 ppm total RE, the *Pyrocypis* sample contained 110 ppm, and the foraminifera 60 ppm RE on a dry weight basis (the RE content of foraminiferal tests from cores was found to be several times lower, and this discrepancy is discussed in the text). Taking

into account the content of plankton in sea-water the RE contained in plankton is only 0.001 to 0.003  $\mu\text{g}/\text{l}$ , i.e. only 0.1% to 0.3% of the total RE of sea-water in the euphotic zone is associated with plankton. Hence biological uptake cannot be an important factor in the conveyance of RE from the surface to deeper water. Adsorption of RE by decaying and sinking biological material may conceivably still play a role (it does with Ba), but no information on it is available.

The eolian contribution to the RE in the Indian Ocean was studied in three samples of solid air suspensions. The RE content of the wind-borne solids ranged from 85 to 170 ppm total RE, similar to that of terrestrial rocks, but this amounted only to 0.001 to 0.0017  $\mu\text{g}$  RE per cubic meter of air. The pore-size of the air filter was not indicated. The authors felt that the eolian contribution of RE to Indian Ocean sea-water was low, and their main source was terrigenous material, as indicated by the high RE content of near-shore waters.

Goldberg et al. (1963), using activation analysis, found 0.011  $\mu\text{g}/\text{l}$  total RE (without Y) in one sample of Pacific sea-water from 100m depth (with Y the RE content would probably have been about 0.017 to 0.022  $\mu\text{g}/\text{l}$ ), and suggested that since in the neutron activation procedure contamination was kept at a minimum, their results should best represent the actual content of RE in sea-water. Later in the same paper they stated that one would

expect significant variations in concentration of RE from one water mass to another. This second statement appears indeed to be corroborated by the differences in values between their data and those of Balashov and Khitrov, since the regularities of the RE distributions found by the latter would seem to outrule the possibility that 99% of the RE contents found by them originated merely in sample contamination. The results given in the two papers seem to show rather definitely that very considerable differences in RE content of different water bodies do exist.

Balashov, Ronov, Migdisov and Turanskaya (1964) collaborated on a paper on the effects of climate and facies conditions on the fractionation of RE in the sedimentary process. The first and the last authors are known for their extensive work on RE in various geological environments, whereas the two others are known for work on the geochemistry of various groups of elements in the sedimentary cycle.

The authors summarized the data on RE distributions in sedimentary materials available at the time their paper was written and pointed out that while averages of the RE in groups of sedimentary samples were rather similar, the RE distributions in single samples in each generic group of sedimentary materials varied widely. They compiled a table of published RE distributions (normalized to La=1) in 3 clays, 3 sandstones, 3 limestones,

2 coals, 3 phosphorites, 2 samples of fish-bone detritus and 3 marine sediments (for the latter only partial data were available), presenting the largest distribution variations found and bringing out mainly that the ratio  $\frac{\sum \text{Ce earths}}{\sum \text{Y earths}}$  varied very widely in each group. Selective depletions or enrichments in Ce, Eu or Y were not noted by them (these become prominent only when normalization of the sample RE to the RE in a reference material is carried out, which they did not do).

On the premise that RE distributions in sediments do vary, they made this study as a first step toward understanding the geochemical behavior of the RE in the sedimentary cycle. They studied the RE in a sedimentary basin around Moscow, on which extensive geological and geochemical information was available. Samples were collected from outcrops of sedimentary rocks formed in the same basin during two different geological periods, in one of which the climate was arid and in the other very humid. Since the igneous source rocks of the sediments were thus the same in both periods, any RE distribution differences found were due only to the difference in climate conditions.

Their results showed as follows:

a) In sands and clays and one carbonate formed in an arid climate the total RE distributions, as measured by the

$\frac{\sum \text{Ce}}{\sum \text{Y}}$  ratio, were statistically identical and the total RE

content was similar in the clays and sands (0.025 - 0.036% RE<sub>2</sub>O<sub>3</sub> in clays, 0.036 - 0.043% RE<sub>2</sub>O<sub>3</sub> in sands, not determined in the carbonate sample). Lacustrine sands were slightly enriched in heavy RE compared to terrestrial ones, and lacustrine clays were slightly depleted in them.

b) In the same sediment types formed under humid conditions, pronounced differences developed: the clays became enriched and the sandstones depleted in RE; the  $\frac{\sum Ce}{\sum Y}$  in the clays became much higher (preferential enrichment in the light RE, probably due to preferential retention of the heavy RE in the ground waters by complexation), in the sandstones it remained roughly the same as in the arid ones and the carbonates (shelf and pelagic) were enriched in the heavy RE. This too pointed to preferential retention of the latter in the water. Both clays and sandstones picked along profiles cutting from the weathering zone in the direction of sediment transport toward the center of the basin which was covered by a sea at the time of formation, showed gradual decrease in the  $\frac{\sum Ce}{\sum Y}$  ratio, again confirming preferential leaching of the heavier RE by ground waters close to the source areas, and eventual deposition of the heavy-RE-enriched pattern on sediments close to the sea and in the sea-water itself, the latter being reflected in the RE pattern in the carbonates.

In four marine sediment samples for which no absolute

RE values are given they found a conforming pattern: sediments in the vicinity of humid tropical areas in India had low  $\frac{\sum Ce}{\sum Y}$  ratios (patterns similar to the 12 marine samples discussed in the main paper), whereas a sample close to an arid area and a sample close to the Antarctic (where again little chemical weathering goes on) had higher  $\frac{\sum Ce}{\sum Y}$  ratios.

A preliminary simple experiment revealed another very interesting aspect of the RE problem - it indicated that the organic fraction of carbonates contains at least 20 times more RE than the carbonate itself and the RE distribution in the organic part is very heavily weighted toward the heavier RE.

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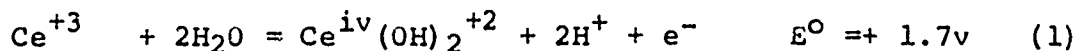
## APPENDIX B

### THEORETICAL CONSIDERATIONS ON THE BEHAVIOR OF Ce and Eu IN THE MARINE ENVIRONMENT.

The thermodynamic data available at present for rare earth elements are still scanty, and those that exist are often of an almost tentative nature. Keeping this in mind it seems, however, of interest to calculate, even though only tentatively, whether and under what conditions we can expect any selective enrichments or depletions of Ce and Eu, the most easily oxidizable and the most easily reducible, respectively, elements of the RE group.

Garrels' sign convention is used in all redox equations.

The prevalent inorganic species of Ce in sea-water solution are most likely to be hydroxyl or carbonate complexes of  $\text{Ce}^{\text{iii}}$  and/or  $\text{Ce}^{\text{iv}}$ . Unfortunately, data are available (in NBS tables) only for  $\text{Ce}^{+3}_{\text{aq}}$ ,  $\text{Ce}^{\text{iv}}(\text{OH})^{+3}_{\text{aq}}$  and  $\text{Ce}^{\text{iv}}(\text{OH})_2^{+2}_{\text{aq}}$ . The standard redox equation governing the relationship of the first to the third species is calculated to be:



At pH 8 in sea-water this results in the half-cell potential:

$$E_h = 0.76 + 0.059 \log \frac{[\text{Ce}^{\text{iv}}(\text{OH})_2^{+2}]}{[\text{Ce}^{+3}]} \quad (2)$$

(Square brackets denote concentrations in moles per liter.)

The ratio of the two species will depend on the Eh of the sea-water in which they occur.

The Eh of sea-water is highest where it is saturated and at equilibrium with dissolved gaseous oxygen. The redox equation of oxygen in water is:



Hence:

$$\text{Eh} = 1.23 + (0.059/4) \log p_{\text{O}_2} [\text{H}^+]^4 \quad (4)$$

The partial pressure of saturated oxygen in sea-water is about 0.25atm, and at pH 8 this gives rise to Eh = +0.75v.

Pelagic bottom waters have been reported at the XXI International Congress of Geology (1960) to cluster around Eh = +0.4v.

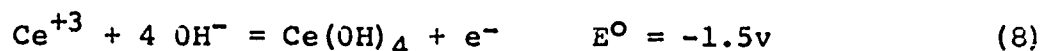
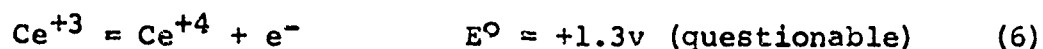
Thus +0.4v to +0.75v is apparently the range of Eh values naturally occurring in sea-water. Correspondingly, the range of ratios of the mentioned inorganic Ce species will be, roughly:

$$\frac{[\text{Ce}^{\text{IV}}(\text{OH})_2]^{+2}}{[\text{Ce}^{+3}]} = 0.7 \text{ to } 10^{-6} \text{ at Eh} = 0.75\text{v to } 0.4\text{v} \quad (5)$$

I.e. this ratio will vary greatly in the range of Eh values known to occur in the sea, and local conditions may hence affect quite strongly the behavior of cerium in the marine environment if these are indeed the predominant inorganic species of cerium in sea-water. Obviously, if carbonated (or sulfated)  $\text{Ce}^{\text{IV}}$  species exist and are more stable than the hydroxylated ones, the picture would change, shifting even more in favor of quadrivalent cerium, which would

behave differently than the other RE. No data on such species are available at present.

A solid cerium compound which can be expected to be important in controlling the behavior of Ce in sea-water is  $\text{Ce(OH)}_4$ , due to its extremely low solubility product. The pertinent equations are:



At pH 8 this results in the half-cell potential:

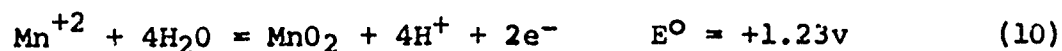
$$E_h = -0.1 + 0.059 \log \frac{[\text{Ce(OH)}_4]}{[\text{Ce}^{+3}]} \quad (9)$$

In the Pacific sea-water on which RE values were reported by Goldberg et al. (1963), a normal value of Ce relative to the other RE would have been about 6 ng/l, or about  $10^{-10.4} \text{ M}$ . According to equation (9) this amount of  $\text{Ce}^{+3}$  would be at equilibrium with pure  $\text{Ce(OH)}_4$  (activity = 1) at  $E_h = +0.51\text{v}$ . I.e. above this  $E_h$  Ce could become depleted in such sea-water merely by precipitation of a pure  $\text{Ce(OH)}_4$  phase. Precipitation of this compound in solid solution in another solid, e.g. in a manganese nodule, where its mole fraction constituted  $x = 10^{-3}$  (as found in the nodule analyzed in this work) would bring it into equilibrium with  $10^{-10.4} \text{ M}$  of  $\text{Ce}^{+3}$  at about  $E_h = +0.34\text{v}$ , and since this is less than the  $E_h = +0.4\text{v}$

found in bottom waters, it is clear that this mechanism alone can cause depletion of dissolved inorganic Ce at all Eh values occurring in sea-water. (Again, another solid compound of Ce<sup>iv</sup>, more stable than Ce(OH)<sub>4</sub>, possibly CeO<sub>2</sub> on which no thermodynamic data were found, might be the most important factor in controlling and reducing the concentration of cerium in sea-water.) Results quoted in the main paper, indicating that more than 90% of cerium in sea-water were associated with solid phases, are well in accordance with these calculations.

The selective cerium enrichment found in manganese nodules raises the question whether their Eh characteristics are directly responsible for this enrichment.

In the nodules the main oxidizing species is MnO<sub>2</sub>. Dissolved inorganic manganese in the sea occurs as Mn<sup>+2</sup> at a concentration of 10<sup>-9</sup>M (Goldberg, 1961). The pertinent redox equation is hence:



at pH 8 and  $\text{[Mn}^{+2}] = 10^{-9}\text{M}$  this gives:

$$\text{Eh} = 0.56 + 0.03 \log \text{[MnO}_2\text{]}$$

I.e. a nodule consisting of pure MnO<sub>2</sub> could coexist with 10<sup>-9</sup>M dissolved Mn<sup>+2</sup> at Eh = +0.56v, and this Eh is only very slightly sensitive to a reduction of the mole fraction of MnO<sub>2</sub> in the

nodule: at  $x_{\text{MnO}_2} = 10^{-2}$  we would still have  $E_h = +0.5\text{v}$ . This  $E_h$  is seen to be somewhat higher than the  $E_h = +0.4\text{v}$  of bottom waters (see above), and thus the microenvironment of nodules will become more depleted in dissolved Ce than any adjacent non-oxidizing phase, and eventually the nodule should concentrate the cerium from surrounding sediments (as suggested by Pachadzhyanov, 1963), whereas the amount of other RE coprecipitated by a manganese nodule is likely to remain at its original value. The enrichment factor of cerium over the other RE under these  $E_h$  conditions would possibly depend on the time available for this process. If local external causes raise the  $E_h$  of the sea-water around a nodule, it will become relatively more enriched in cerium, and as the local  $E_h$  varies, the enrichment factor of Ce relative to other RE will vary correspondingly. The extent of enrichment will be governed by equation (9) or by an analogous equation involving the actual solid compound of  $\text{Ce}^{\text{IV}}$  which occurs in solid solution in the nodules.

The above considerations indicate that cerium in the marine environment can be expected often to behave differently from the other RE, and thus be a sensitive indicator of local  $E_h$  variations in it.

The natural  $E_h$  range of sea-waters was seen above to be relatively oxidizing. Under such conditions the fraction of Eu in divalent state is extremely low:



$$Eh = -0.43 + 0.059 \log \frac{[\text{Eu}^{+3}]}{[\text{Eu}^{+2}]} \quad (13)$$

Hence, roughly,  $[\text{Eu}^{+3}] / [\text{Eu}^{+2}] = 10^{14}$  to  $10^{20}$  at  $Eh \approx +0.4\text{v}$  to  $+0.75\text{v}$ . The fractions of  $\text{Eu}^{+2}$  in this  $Eh$  range are seen to be so low that no fractionation can be detectible. Analytical data on RE in materials in the marine environment bear out this conclusion; no selective Eu depletions nor enrichments were observed.

Only in environments where the redox potential drops to  $Eh \leq -0.3\text{v}$ , thus producing the ratio  $[\text{Eu}^{+3}] / [\text{Eu}^{+2}] \leq 100$  can the  $\text{Eu}^{+2}$  become noticeably involved and result in selective enrichments or depletions of Eu. In buried marine sediments the  $Eh$  is reported to drop to not lower than  $-0.2\text{v}$ , which is insufficient to produce such effects.

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APPENDIX C

CHEMICAL YIELDS<sup>#</sup> OF Ce<sup>139</sup> AND Y<sup>88</sup> IN RE GROUP SEPARATION

Table C-1

Sample	Chemical Yield, %	
	Ce <sup>139</sup>	Y <sup>88</sup>
V5	100	97
V2	99.5	99.5
V9	91.5	95.5
V6	54.5*	53.5*
E2	85	83
E9	61	55.5
A1	80	92
A2	63	61.5
A3	77.5	88.7
A4	68.5	66
A1C	49	54
A2C	71.5	71.5
A3C	81.5	84.5
A4C	69	67
A1K	64.5	65
Blank C	87	not added
Oolite	92	91.5
Shell	not added	76
Bone	55.5	56.5
Clam	43	45
Nodule	88	91
SW	69	69
MPS	88	86.5
MPS Blank	not added	90
OM	82	99
Carbonatite	90	98

# The chemical yield of Y<sup>88</sup> was used in calculating the concentrations of all the RE except cerium.

The chemical yield of cerium was monitored separately by Ce<sup>139</sup> since the singularly easy oxidizability of this element under the experimental conditions of the procedure could result in its behavior differing from that of all the other RE.

\* low yield due to spillage.

APPENDIX C

DETAILS ON ASSIGNMENT OF SOME BLANK VALUES

The sea-water fractions were the only ones to have blanks constituting a considerable percentage of the gross value, from 5% up to 50%, or possibly more, and the uncertainty of the blank values contributes highly to the overall uncertainty of the net values. The high uncertainty of the blanks is mainly due to the low count-to-background ratio for such low amounts; low background equipment was not available at the time. The blank of MPS (=MPB) included, besides reagents, a Millipore filter like the one on which the MPS suspended solids had been filtered out of the sea-water, and was run through the chemical procedure concurrently with the MPS. To get "MPS net" its values were subtracted from "MPS gross" and the errors of both were combined appropriately.

No concurrent blanks were run for SW or OM, and the assignment of blank values to subtract from them was based on the following reasoning. The silicate blank values (Table 2) are 5 to 10 times higher than the carbonate blank (=BlC) values (Table 3) except for La, and the La value is about 20 times higher than that of MPB (Table 5). This was straight proportional to the total volumes of reagents in them. (Surprisingly, the distilla-

tion of reagents through vycor glass seems not to have reduced the RE concentrations very much). The blank values for SW and OM were therefore based on the volume of reagents used in processing them. About 185 ml total liquids had been used for SW and about 90 ml for OM, hence we assigned 1.5 BIC for SW, and 0.75 BIC for OM. The uncertainty of this speculation was expressed in a  $\frac{2}{3}$  blank error allowed :  $(1.5 \pm 1)$  BIC and  $(0.75 \pm 0.5)$  BIC. The true blanks most probably fall well within these ranges.

Tm and Lu were selectively high in BIC, so for them  $(3 \pm 2)$ MPB and  $(1.5 \pm 1)$ MPB values were used as the next best choice. The relatively high values of Sm, Eu, Dy, Y in MPB compared to BIC indicate that the Millipore filter contributed RE of this order of magnitude; for cases where no filter was included these values were therefore too high, probably.

La seems to occur as a special selective contaminant, seeing its high values both in BIC and in SW and OM; wider range formulas were therefore used for it:  $\frac{1.5 \text{ BPC} + 3 \text{ MPB}}{2} \pm \frac{1.5 \text{ BPC} - 3 \text{ MPB}}{2}$ . Even so, the final La values in OM and SW are quite questionable. All the other SW and OM values though not good enough to determine uniquely a distribution pattern line, are certainly well within a factor of 2 from their true values, and can serve as an adequate basis for the guarded conclusions drawn from them.

APPENDIX D

ACKNOWLEDGEMENTS

I wish to express my deepest gratitude to Professor John W. Winchester to whom I will always feel indebted for the most outstanding scientific and personal relationship that a teacher could offer a student. His enabling me to come to M.I.T., his initiating my interest in the geochemistry of the rare earths, his optimistic, warm encouragement and personal collaboration, advice and help throughout my years of graduate study and research work have been of inestimable value to me and will always be treasured.

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I wish to express here my gratefulness to my dear mother,

Mrs. Chaya Volfovsky, who from near and far helped me on my way to this achievement, to Mrs. Clara Pupiski, who helped me greatly in the final stages of this work and, above all, to my husband, Rabbi Charles Spirn, without whose encouragement, understanding, guidance and selfless helpfulness this work could not have been completed.

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BIOGRAPHICAL NOTE

The author, Regina Volfovsky Spirn, was born in Wilno, Poland, on April 10, 1934, the daughter of Chaya Lew and Nahum Volfovsky. Her elementary education was intermittent due to German occupation during World War II and subsequent migration as a refugee. She arrived in Israel in 1947 where she attended the last grade of elementary school and completed her secondary education at the Tel Aviv Municipal High School "G", and graduated as valedictorian of her class in 1952. She attended the Chemistry Department at the Hebrew University of Jerusalem from November 1952 to September 1957, where she won First Prize in the University Scholarship competition upon entering and held the award throughout her attendance. She received the degree of Master of Science in Chemistry in April, 1958. The subject of her Master's Thesis was: "The reaction of bromine with ammonia in aqueous solution." From September 1957 to April 1958, she worked as a Research Physical Chemist in the Geology division of the Israel Commission of Atomic Energy, and, from May 1958 to May 1961, as Research Geochemist at the Geological Survey of Israel.

In August 1961, the author entered the Department of Geology and Geophysics at M.I.T. as a Research Assistant graduate student and remained in this position until completion of her work in September 1964. At M.I.T. she was elected to membership in the Society of Sigma Xi. She also holds membership in the Geochemical Society.

The author was married to Rabbi Charles A. Spirn of Yonkers, New York, in October, 1964.